Characterisation and Valorisation of Fluoride-Rich Sludge from Aluminium Industry

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the degree

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in

Process Metallurgy

by

DEVAYANI DUDHARAM NAKADE (MT23PME003)

under the guidance of

Dr. Y. Y. Mahajan (Supervisor)
Dr. A. B. Rathod (Co-Supervisor)
Dr. P. Y. Deshmukh (Co-Supervisor)

Department of Metallurgical and Materials Engineering
Visvesvaraya National Institute of Technology
Nagpur 440010 (India)

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Department of Metallurgical and Materials Engineering

Visvesvaraya National Institute of Technology, Nagpur

Declaration

I, Devayani Dudharam Nakade, hereby declare that this dissertation titled "**CHARACTERISATION AND VALORISATION OF FLUORIDE-RICH SLUDGE FROM ALUMINIUM INDUSTRY**" is carried out by me in the Department of Metallurgical and Materials Engineering of Visvesvaraya National Institute of Technology, Nagpur. The work is original and has not been submitted earlier in whole or in part for the award of any degree/diploma at this or any other Institution / University.

Devayani Dudharam Nakade

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Dr. Y. Y. Mahajan Assistant Professor MME, VNIT Nagpur	Dr. A. B. Rathod Assistant Professor MME, VNIT Nagpur	Dr. P. Y. Deshmukh Manager R&D Minex Metallurgical Co. Ltd. Nimji, Nagpur

Dr. D. R. Peshwe
(Head of Department)
MME, VNIT Nagpur

VISVESVARAYA NATIONAL INSTITUTE OF TECHNOLOGY NAGPUR

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Devayani N	Characterisation and Valorisation of Flu...	15%		2682790945	23-May-2025

Name Devayani Dudharam Nakade
Enrollment No: MT23PME003
ID No: 30802

Dr. Y. Y. Mahajan
Assistant Professor,
Department of Metallurgical & Materials Engineering
VNIT, Nagpur

Dr. A. B. Rathod
Assistant Professor,
Department of Metallurgical & Materials Engineering
VNIT, Nagpur

Dr. P. Y. Deshmukh
Manager R&D
Minex Metallurgical Co. Ltd, Nimji, Nagpur

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VNIT, Nagpur
Date:

Ms. Devayani Dudharam Nakade
(MT23PME003)

ABSTRACT

Aluminium alloys find its application in various sectors such as transportation, packaging, electrical and electronics. It is used in orthopaedic implants, prosthetics, and surgical instruments due to its lightweight, durable nature and ease of sterilisation. With the rapid industrialisation and unique set of properties of Aluminium alloys, it demand in society is at peak. This also leads to the production of harmful by-products such as sludge, PAF, etc. Disposal of sludge waste has become a very serious environmental issue in the present 21st century, as it leads to anthropogenic activities. The waste produced by Aluminium master alloy producing industries contains fluorides, which is a serious concern from environmental point of view. Sludge containing 40 (w/w)% Fluoride adversely affects the environment. Such Fluoride-containing waste is disposed of in the environment in an untreated condition, then it causes hazardous issues for living organisms. Fluorine from the sludge, when dissolved in drinking water, makes the water unsuitable for living organisms. When Fluorine level exceeds 1-1.5 mg per litre in drinking water leads to parathyroidism and some neurological disorders in human beings. So, in this research, the fluoride sludge collected from the Aluminium industry is studied. The characterisation of the sludge is carried out by various techniques such as SEM, XRD, XRF etc. Valorisation of the fluoride-containing waste is discussed with mass balance study. The efforts are also taken to explore the potential use of Sludge in acid manufacturing and composites.

(KEYWORDS: Fluoride, Sludge, anthropogenic, potential, Aluminium, master alloys)

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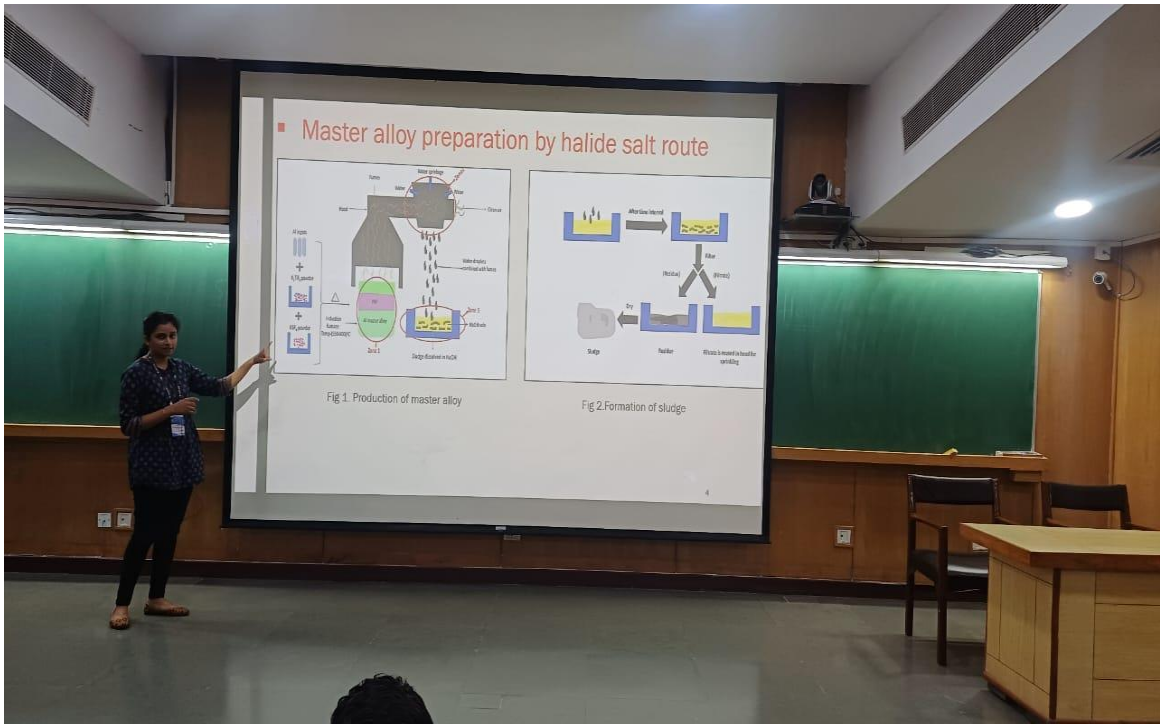
LIST OF ABBREVIATIONS

PAF	**Potassium Aluminium Fluoride**
TPR	**Thermo-reduction route**
PMR	**Powder Metallurgy route**
AMR	**Arc melting route**
MP	**Melting point**
DTA	**Differential Thermal Analysis**
SEM	**Scanning Electron microscopy**
DTA	**Differential Thermal Analysis**
WD-XRF	**Wavelength Dispersive X-ray Fluorescence**
XRD	**X-ray Diffraction**
UDS	**Untreated dry sludge**
M.A.	**Master Alloy**

PUBLICATIONS

1)Successfully presented a paper titled **"Valorisation of Fluoride containing Industrial waste"** at the **National Symposium of Research Scholars on Metallurgy and Materials 2025 (NSRS 2025)** organised by the **Indian Institute of Technology, Kanpur.**



Oral Representation of the paper at NSRS 2025, IIT Kanpur.

2) The research paper has been drafted based on the present thesis work and is intended for submission to journal:

Paper Title:

"Characterisation and Valorisation of Fluoride-Rich Sludge from Aluminium Industry"

The paper is planned to be submitted to one of the following reputed journal in the field of Materials Science and Technology:

1)Journal of Alloys and Compound (Elsevier)

2)Journal of Hazardous Materials (Science Direct)

3)Journal of Material Processing Technology (Elsevier)

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CHAPTER 1

INTRODUCTION

Chapter 1 has discussed the linking of day-to-day life the materialistic things, and the importance of materials in human life. It has emphasised the importance of the circular economy in it. Besides, the production process of Aluminium master alloy has been discussed, and the path in the process through which waste is formed during master alloy preparation has been highlighted.

1.1 General Background

In day-to-day life, we do various activities like exercising, travelling, cooking, playing, packaging, etc. Now, all the activities mentioned here cannot be solely done without help of any equipment or material. That material may be from a class of material such as polymer, metal, ceramic or composite. Now, the properties which this class of material possess is different from each other, and their functions also differ from each other. Likewise, their method of production also differs. Different production methods are used for the production of these materials. Since the processes are brought into the practice, it is very obvious that the byproducts may also be formed. Some byproducts of the reaction may be useful, may have some applications, but some may merely have any discovered application, and these byproducts with unexplored applications and reuse potential are termed as waste products. This unexplored reuse potential and application of the by-products affects the process by various ways:

1) Makes the process less efficient

2) Wastage of resources

3)Environmental pollution

4)Scarcity of resources for upcoming generations

5) an unexplored area of research from where we may benefit economically and literally after exploration[1]

And the foremost benefit of the processing of the waste is to Mother Earth, which preventz it from becoming trash. So, to deal with these problems or to get up on these problems, we need not only peep but to dive into the world of waste and need to get the solution of the unsolved queries.

1.1.1 Role of Circular Economy in Aluminium production

Today's economy has mainly emphasised on the circular economy, which means a system designed to keep resources in use for as long as possible, minimising waste and maximising resource efficiency. Let us take one example for the emphasisation of circular economy i.e. Aluminium production from the waste. It has been found that extracting Aluminium from bauxite is not economical and affordable. Recycling aluminium uses 95% less energy than producing aluminium from raw materials. It also saves 97% of greenhouse gas emissions produced in the primary production process. Recycling 1 tonne of aluminium saves 9 tonnes of CO2 emissions and 4 tonnes of bauxite.[1], [2], [3] So, utilising waste to get some valuables is a way of making the process more efficient. So, one of the wastes that is to be targeted is dry sludge, which comes as a by-product of Aluminium master alloy preparation.

1.1.2 Importance of Al Master Alloy

Master alloys play a crucial role in modern metallurgy and have a significant impact on our daily lives, often behind the scenes. These are combinations of metals used to introduce specific elements into a melt, improving properties like strength, corrosion resistance, or castability in the final alloy. From the lightweight aluminium alloys in smartphones and vehicles to the durable materials used in kitchen appliances, electronics, and even medical devices, master alloys help tailor metal properties to meet everyday performance needs. By enabling more efficient and precise alloy production, master alloys contribute to the quality, durability, and sustainability of the products we use every day. Aluminium master alloy is prepared and added in the pure aluminium as an alloying agent, which acts as grain refiner. This has enhanced properties from those of pure aluminium like strength, corrosion resistance, machinability, ductility, hardenability, etc. Thus, various additions usually done in Al alloys are Si, Cu, Mn, Sr, Zn, Ti, B etc. for the specific set of properties[4].

Al-Si: Used to increase the silicon content in aluminium alloys, improving casting properties and machinability.

Al-Mn: Improves strength and corrosion resistance, particularly in low-strength applications.

Al-Cu: Increases strength and hardenability, commonly used in engineering applications.

Al-Mg: Provides good strength and corrosion resistance, particularly in aerospace and transportation.

Al-Ti-B: Used as a grain refiner to control the grain structure of aluminium alloys.

Al-Sr: Modifies the morphology of silicon in aluminium-silicon alloys, enhancing ductility and machinability.

Al-Zn: Increases strength and hardenability, commonly used in automotive and construction applications..

1.2 Overview of Master Alloy production

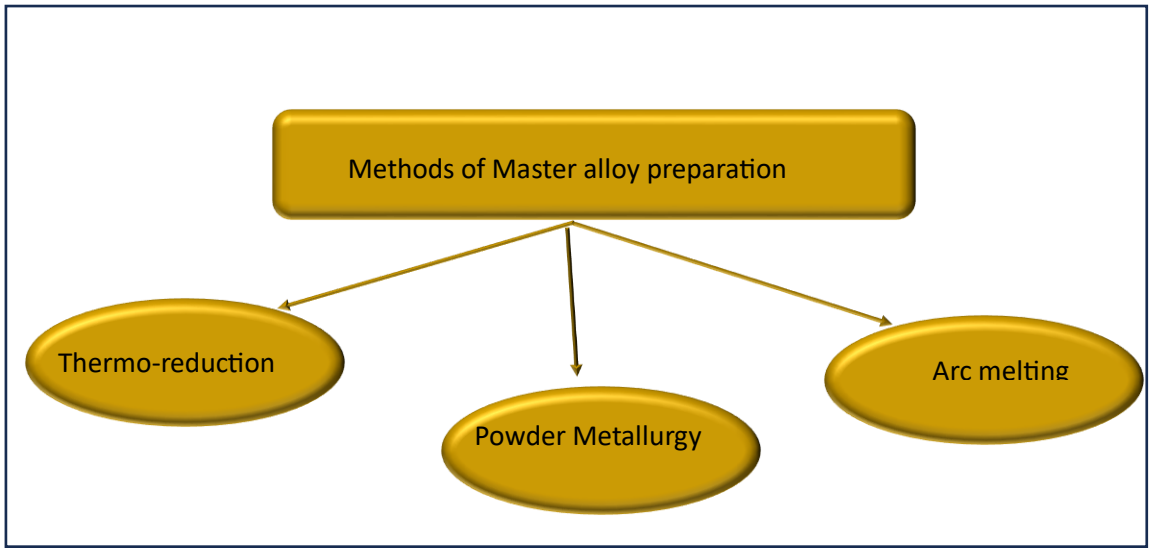

Figure 1.1: Routes of master production

Among all these master alloys, TiBAl alloy is most prevalent and commercially used. Ti-B-Al can be prepared by various routes. Depending upon the type of input material and the method of preparation, the byproducts vary. Master alloys are prepared by various methods, including thermos-reduction, powder metallurgy, and arc melting. Thermo-reduction involves the reduction of oxides or salts of alloying elements using a reducing agent, like aluminium or magnesium. Powder metallurgy involves mixing elemental or pre-alloyed powders, which are then compacted and sintered. Arc melting uses an electric arc to melt the alloying elements in a controlled atmosphere[4].

1.2.1 Powder Metallurgy Route

Through the powder metallurgy route, various benefits can be gained, such as precise control over composition and microstructure, complex shapes can be fabricated, and near near-net shape process. But it has various shortcomings also. It is a time-consuming process and has a high initial cost since the equipment required for the production through powder metallurgy is expensive. Besides this, there is batch-to-batch variability in chemical composition, and the process is prone to porosity.[5]

Table 1.1: Merits and Demerits of the TiBAl production through PMR

Merit	Demerit
Microstructure Control	High Initial Costs
Complex Shape Fabrication	Potential for Porosity
Enhanced Properties	Batch-to-Batch Variability
Material Efficiency	Time-Consuming

1.2.2 Arc Melting Route

Arc melting is the process whereby using electric arc is used between the tungsten and the metal being melted, and the desired alloy is produced. This method is particularly used for high melting point metals like titanium, and can be done in a vacuum or inert atmosphere to prevent oxidation. Arc melting offers advantages like rapid production, homogeneity, and

the ability to melt reactive metals . Care must be taken to avoid the cathode touching the sample during the melting process, as this can lead to contamination or damage[5].

Table 1.2:Merits and Demerits of the TiBAl production through AMR

Merit	Demerit
High Purity	Potential for Boron Loss
Versatility	Homogeneity Issues

1.2.3 Thermo-Reduction Route

Thermo-reduction route is the way of master alloy preparation, which falls under pyrometallurgy. It uses high temperature to reduce Titanium and Boron salts in the presence of Al. The advantages of using this process for the production of Master alloy is that high-purity master alloy can be produced by gaining control over the alloy

composition. This process has potential for having control over the chemical composition by having control over reaction pressure, temperature, time, etc. And also, by controlling stoichiometry and by homogeneously mixing the reactants by agitating the bath. Also, this route is cost-efficient. Now, every coin has two faces. Likewise thermo-reduction route also has disadvantages along with advantages. It is disadvantageous as there are chances of the reoxidation of the metal, and is energy-consuming since without reaching particular temperature the process actually does not begin. Also, this process as involves high temperatures, high energy consumption it has potential safety hazards also sticked with it[4]. One more hazard is that 45-50% fluoride containing waste is generated.

Table 1.3: Merits and Demerits of the TiBAl production through TRR

Merit	**Demerit**
High Purity	Safety hazards
Cost efficient	Energy consuming
Potential for control over alloy composition	Impurity incorporation due to re-oxidation

Among all three routes, thermo-reduction is the most common route. The process of master alloy production begins with putting two halide salts, either K_2TiF_6 and KBF_4 or Na2TiF6 and NaBF4, along with pure Al ingots into the induction furnace. An induction furnace consists of a non-conductive crucible holding a charge of metal to be melted, surrounded by a metallic coil. When current is passed through the coil, eddy currents are induced. These eddy currents, when passing through the conductive metal and salts, heat it by Joule heating. Once the metal and halide salts are melted, the eddy current causes vigorous stirring of the melt, assuring the good mixing of metal and salts. After the mixing of salts and the metal, a reaction occurs between them and the products TiBAl and PAF or cryolite is formed.

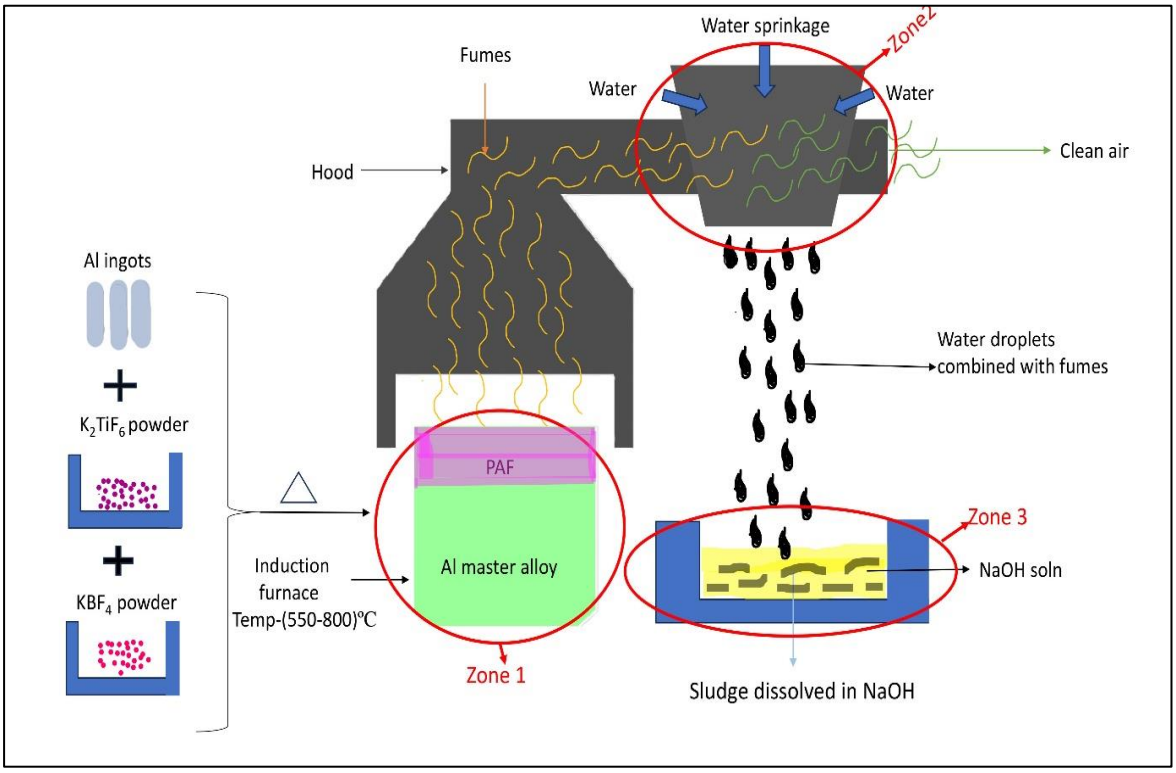

Figure 1.2: Production of Master alloy through TRR.

The upper layer PAF is removed by the hopper until the shiny metallic surface is seen, and then the furnace is tilted and the master alloy is cast. In zone 1 reaction between salts and the aluminium takes place. In zone 2 PAF particles that enter the hood get wetted by water and due to heavy weight, the slurry falls. Zone 3 contains the NaOH solution which is there to neutralise the acidic slurry falling from zone 2.

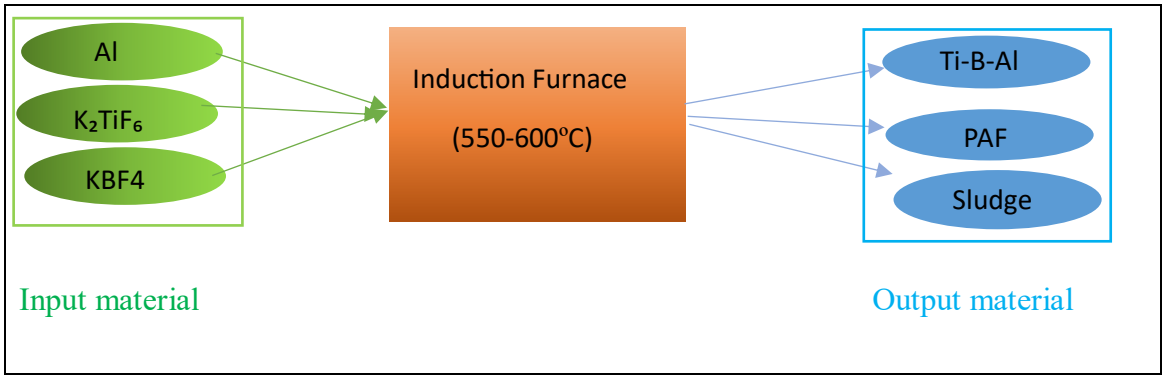

Figure. 1.3: Reactant to Product conversion

1.3 PAF and Sludge as Byproduct

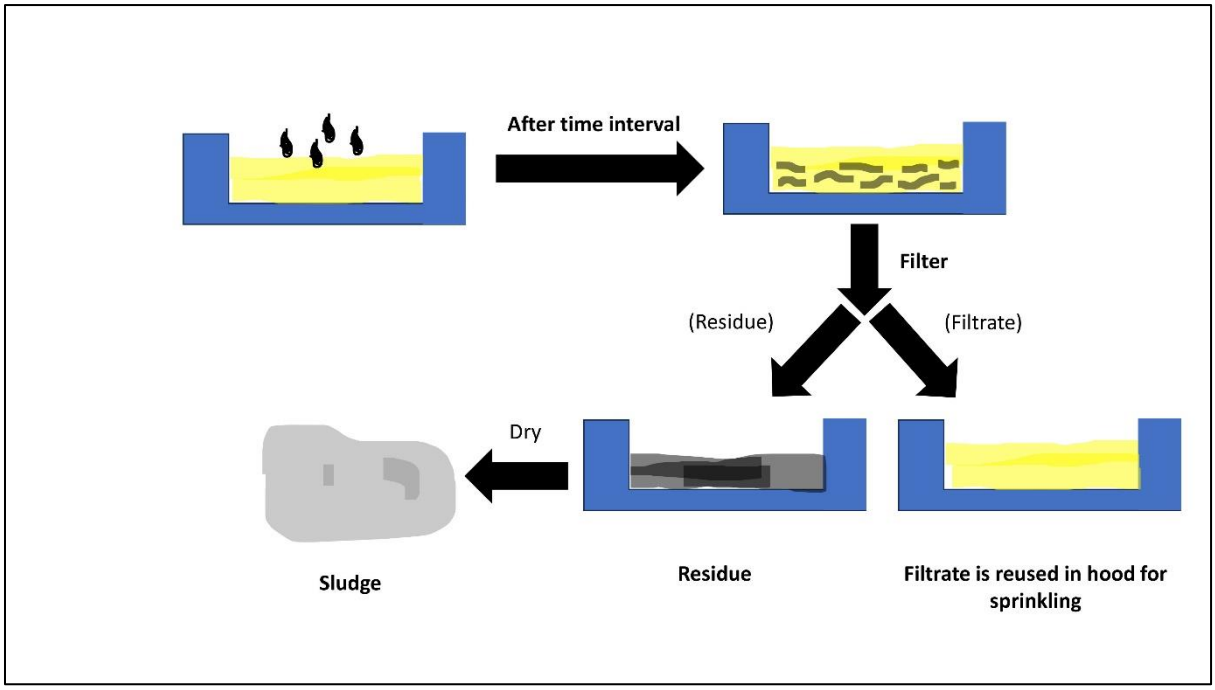

Figure. 1.4.: Outcome of Sludge as a byproduct in TRR

During the production of TiBAl master alloy by the thermo-reduction, a byproduct, cryolite or Potassium Aluminium Fluoride (PAF) and sludge are also produced depending upon the input halide salts. This aluminium Fluoride (PAF) has good resale value but the utility potential of Sludge which is formed due to the reaction of the PAF with the caustic soda, was not yet explored. Sludge is one of the byproducts of master alloy production. When a TiBAl master alloy is prepared using the melting route of halide salt two byproducts, PAF and Sludge, are formed. TiBAl is the desired product and PAF/cryolite is a byproduct. Out of PAF and cryolite, both have good resale value. PAF has good resale value since it has applications in welding work. And cryolite has application in the Aluminium industry Aluminium industry Cryolite is used along with fluorspar to bring down the M.P. of Alumina and thus makes the process more efficient by melting Alumina at a lower temperature. Now, as PAF is formed, being fine and having a density lesser than metal it floats on the master alloy. It is periodically removed from the induction furnace till the master alloy surface is seen. During all these processes, some fine PAF particles goes with the gases in the hood. This flow of dust particles with the gases cannot be directly emitted in the atmosphere so water is sprinkled over the fumes and dust particles being wetted get heavy and fall down and are collected in the NaOH pool below which is there to neutralise the acidic water slurry falling down. After a course of time the neutralised slurry is filtered and we get the residue as sludge. The filtrate is reused for

settling down the dust particles from hood. Since the utility and usage potential of the sludge is yet to explore, the present work is devoted to explore the utilisation potential of the "Dry Sludge."

Objective of Present Work:

1)The current research focuses on exploring the hidden utility potential of the fluoride-containing industrial waste.

2)It focuses on the characterisation of the fluoride-containing industrial waste.

3) It focuses on studying the process with respect to mass balance.

4)It focuses on use of Sludge for making the composites.

CHAPTER 2
LITERATURE REVIEW

Chapter 2 is enriched with the discussion of use of which salt is more efficient while producing the TiBAl, and has also discussed the characterisation of the salts. Beside this it is discussed what would be the probable mechanism going inside the salt and Al bath, what would be the possible reaction going on in between the Al and salts.

2.1 Introduction

Aluminium is a lightweight, soft material in its pure state. Its strength is so low that it cannot withstand heavy loads or stress. So, grain refiners are added to it to reduce the grain size of the aluminium and make it strong. Thus, master alloys have huge and vast applications. They strengthen the material and make it corrosion-resistant.

2.2 Master Alloy by Thermo-Reduction Route

Master alloys such as TiBAl are often humbly synthesised through the thermoreduction process. This method utilises halide salts like potassium tetrafluoroborate (KBF_4) and potassium hexafluorotitanate (K_2TiF_6) as sources of boron and titanium, respectively. Melted aluminium is gently combined with these salts, acting as a reducing agent and a solvent. Within the aluminium matrix, intermetallic compounds like TiB_2 and $TiAl_3$ are modestly formed when titanium and boron are reduced from their salt forms. The entire reaction as understood, takes place at elevated temperatures, typically around 600-650ºC, and is exothermic in nature. The resulting TiBAl master alloy graciously contains finely distributed TiB_2 particles that enhance the mechanical properties and grain refinement of aluminium alloys[4], [6], [7].

2.2.1 Criteria for Selection of Fluoride Salts

By using thermo-reduction TiBAl can be produced by different halide salts made of potassium and sodium. Sodium salts like Na_2TiF_6 and $NaBF_4$ can also be commercially be used but some shortcomings such as the efficiency of the process decreases due to less ability of NaBF4 to

release the Boron atoms in the Al melt. As experimented by Donaldson and Squire, the below table is suggested for the Boron and Titanium releasing efficiencies by K_2TiF_6, KBF_4, Na_2TiF_6 and $NaBF_4$ in different conditions[8]. Tables below are confirmed by analysis of slag formed during the preparation of the Al master alloy.

Table 2.1 Titanium -Boron transfet efficiency for laboratory scale melts

Melt system	**Ti transfer efficiency (%)**	**B transfer efficiency (%)**
c-Al	-	35
KBF_4-Al	-	65
Na_2TiF_6-Al	85	-
K_2TiF_6 -Al	95	-
Na_2TiF_6-Al	95	65

Table 2.2 Titanium and boron exchange efficiencies for large-scale melts.

Melt system	**Ti transfer efficiency (%)**	**B transfer efficiency (%)**
$NaBF_4$-Al	-	15
Na2TiF_6-$NaBF_4$-Al	80	54
K_2TiF_6 -KBF_4-Al	80	89

Above table provides us proof why potassium salts are used as alternative for sodium salts while preparation of the TiBAl master alloy through thermo-reduction though the advantages of using sodium salts are :

1)High resale value having sodium cryolite slag is produced.

2) The amount of sodium salts required are less in weight than the potassium salts used to produce the master alloy if efficiencies of Boron and Titanium released are assumed to be same for both sodium and potassium salts.

3) Slag produced by using potassium salts has higher weight than the slag produced by sodium salts.[8]

Considering all above parameters the potassium salts are used commercially. Hence, slag produced during master alloy production using potassium salts is chosen for study.

2.3 Effect of Temperature on Fluoride Salts (K_2TiF_6 & KBF_4)

K. V. S. Prasad et al. analysed XRD data. Later, they presented extensively DTA study on the dissociation of salts at higher temperatures.

2.3.1 Dissociation Studies of Salts

In order to elucidate the behaviour of the potassium salts K_2TiF_6 and KBF_4, a comprehensive examination was conducted by Prasad et al. utilising Differential Thermal Analysis (DTA) within an inert argon atmosphere across varying thermal conditions, specifically at 400ºC, 575ºC, 650ºC, and 800ºC. The aforementioned salts were subjected to these thermal conditions for an approximate duration of 15 minutes, during which their dissociation characteristics were investigated through the analysis of X-ray Diffraction (XRD) patterns corresponding to the salts maintained at the respective temperatures. The composition of titanium and fluorine within the K_2TiF_6 salt at ambient temperature was found to align with the theoretical stoichiometric ratios of the salts. Notably, the mass loss of the salt exhibited a direct correlation with the elevation of temperature. Remarkably, the analysis of titanium did not indicate any depletion of titanium throughout the heat treatment; however, the fluorine content in the salt diminished by approximately 13% upon heating to 800°C. Additionally, the formation of oxyfluoride was observed up to 800ºC, resulting from the decomposition of K_2TiF_6. The compound K_2TiF_6 was not observed to dissociate into KF and TiF_4 within the temperature range investigated, specifically from 400ºC to 800ºC. This assertion is substantiated by the X-ray diffraction (XRD) analysis of the salts at various temperatures. Up to 858°C, KF remains stable in a solid state, while TiF_4 undergoes sublimation at 285°C. Consequently, should K_2TiF_6 undergo dissociation, the presence of at least KF would be anticipated in the XRD patterns of the thermally treated K_2TiF_6 , a phenomenon not evidenced in the current study. The KBF_4 salt was subjected to thermal treatment at temperatures reaching 800°C. The XRD analysis of the salt treated at 300°C corroborated a reversible transition from the orthorhombic to the cubic phase of
[9].

The differential thermal analysis (DTA) investigation concerning the combination of K_2TiF_6 and KBF_4 did not exhibit any supplementary peaks when compared to the discrete DTA profiles corresponding to the individual salts. Nevertheless, the presence of a third endothermic peak (at 562°C) identified in the DTA profile of K_2TiF_6 was notably absent in the DTA profile of the composite salt mixture. This observation implies the occurrence of a reaction between K_2TiF_6 and KBF_4 at thermal conditions surpassing 465°C. The X-ray diffraction (XRD) pattern derived

from the resultant product of this reaction reveals the existence of both aluminium and $TiAl_3$ phases. The interaction of K_2TiF_6 with molten aluminium facilitates the liberation of titanium, which subsequently integrates into the aluminium matrix. When the solubility threshold of titanium within the liquid aluminium at the specified reaction temperature is surpassed, $TiAl_3$ precipitates in accordance with the Al-Ti phase diagram. Therefore, a minimum reaction temperature of 728°C appears to be essential for the synthesis of Al-Ti master alloys necessary for grain refinement when the mixture is subjected to a heating rate of 20°C per minute. In the context of commercial master alloy production, wherein the conventional methodology involves the addition of the salt to molten aluminium, it is anticipated that this minimum temperature may be slightly lower. The current findings also suggest that KBF_4 engages in a reaction with aluminium at temperatures below the melting point of aluminium, whereas K_2TiF_6 exclusively interacts with molten aluminium. The absence of any dissociation products for both K_2TiF_6 and KBF_4 implies that during the production of master alloys, aluminium interacts directly with these salts rather than with their dissociation byproducts. Furthermore, given that K_2TiF_6 is immersed in liquid aluminium during master alloy production, the likelihood of the formation of K_3TiOF_5 is considerably reduced. Therefore, a direct interaction between aluminium and the respective salts transpires, culminating in the synthesis of $TiAl_3$ and TiB_2. Upon the amalgamation of aluminium with both salts concurrently, no novel peaks were detected in the Differential Thermal Analysis (DTA) investigation. The secondary exothermic peak (at 558°C) exhibited greater intensity than that recorded for the combination of aluminium and KBF_4. The exothermic peak identified at 728°C for the combination of aluminium and K2 TiF6 was absent when aluminium was combined with KBF_4 and K_2TiF_6. The X-ray Diffraction (XRD) profile of the aforementioned mixture subjected to heat treatment at 750°C reveals the existence of TiB_2 and $TiAl_3$ phases in conjunction with aluminium. [9], [10]. The second exothermic peak (at 558°C) was found to be more intense than that for the mixture of aluminium and KBF_4. The exothermic peak that was observed at 728°C for a mixture of aluminium and K2 TiF6 was not observed for aluminium with KBF_4 and K_2TiF_6. The XRD pattern of the above mixture heat treated at 750°C shows the presence of TiB_2 and $TiAl_3$ phases along with aluminium. Thus, the results of the present work confirm the metastable nature of AlB_{12} in the presence of titanium. It appears that KBF_4 reacts with aluminium first and forms AlB_{12} which is then replaced by TiB_2 and $TiAl_3$ due to a subsequent reaction with K_2TiF_6. The present work suggests that the reaction temperature required for the production of ternary Al-Ti-B master alloy is lower than that required for the production of binary Al-Ti master alloy[9].

2.4 Master Alloy as a Grain Refiner

Since the discovery of the Al-Ti-B grain refiner, humble researchers have suggested a few mechanisms for the grain refinement process. The foundation of this grain refinement mechanism appears to either encourage the nucleation of Al grains or limit their growth following nucleation. One of the initial methods proposed for grain refinement involves the undercooling effects of alloying elements, specifically titanium in this scenario, as the boron concentration in solution is quite minimal when titanium is present. Additionally, the other approach relies on the heterogeneous nucleation of Al grains on TiB_2, either directly or indirectly via Al_3Ti present on its surface[11], [12]. The low levels of boron and titanium in the finished castings, however, have prevented any direct observations from being documented. Borides and aluminides are the two types of particles found in master alloys of aluminium. Although the aluminide's identity as Al_3Ti is undeniable, the borides have been determined to be a solid solution of TiB_2 and AlB_2 with a variable Ti/Al ratio. The exceptional stability of the borides in aluminium is the primary reason they are typically regarded as TiB_2. Compared to boride, Al_3Ti is less stable in aluminium. In aluminium, Al_3 Ti dissolves in a matter of seconds, as previously observed. Therefore, the presence of boron in the form of boride particles is thought to facilitate the nucleation of Al grains.

Understanding the stability of TiB_2, the development of a solid solution of TiB_2, AlB_2 and the crystallographic link between the boride phases and Al_3Ti in aluminium is therefore crucial. Boride stability is lower for Al_3Ti. In aluminium, Al_3Ti dissolves in a matter of seconds, as previously observed. Therefore, it can be said that the presence of boron in the form of boride particles promotes the nucleation of Al grains.

Therefore, it is critical to comprehend the crystallographic interaction between the boride phases and Al_3Ti in aluminium melt, as well as the stability of TiB_2 and the creation of the TiB_2 and AlB_2 solid solution. On the surface of the TiB2 particle, there is a coating of Al_3Ti. According to some experts, the surface of the TiB2 particle has a single layer of titanium atoms. Additionally, it was asserted that Al_3Ti is in charge of the nucleation of Al grains and that it is accountable for the nucleation of Al grains under a TEM[12], [13].

Using the Z-contrast approach, it was seen under a TEM. These assertions overlooked a crucial aspect of the microstructure of Al-Ti-B master alloys: small TiB_2 particles are forced into the Al grain borders, while giant compounded particles of TiB_2-Al_3Ti are found in the -Al grain centres. A stable phase on the surface of TiB_2 particles causes the agglomeration of Al_3Ti and a

small amount of TiB_2 particles, while a large population of the TiB_2 particles is pushed into the -Al grain boundaries, according to X. Wang and Q. Han, who also noted that the distinctive microstructure of Al-Ti-B master alloys shows this. Al_3Ti on the surface of TiB_2 is generally thought to be the cause of -Al nucleation in grain refining. It should be mentioned as well.

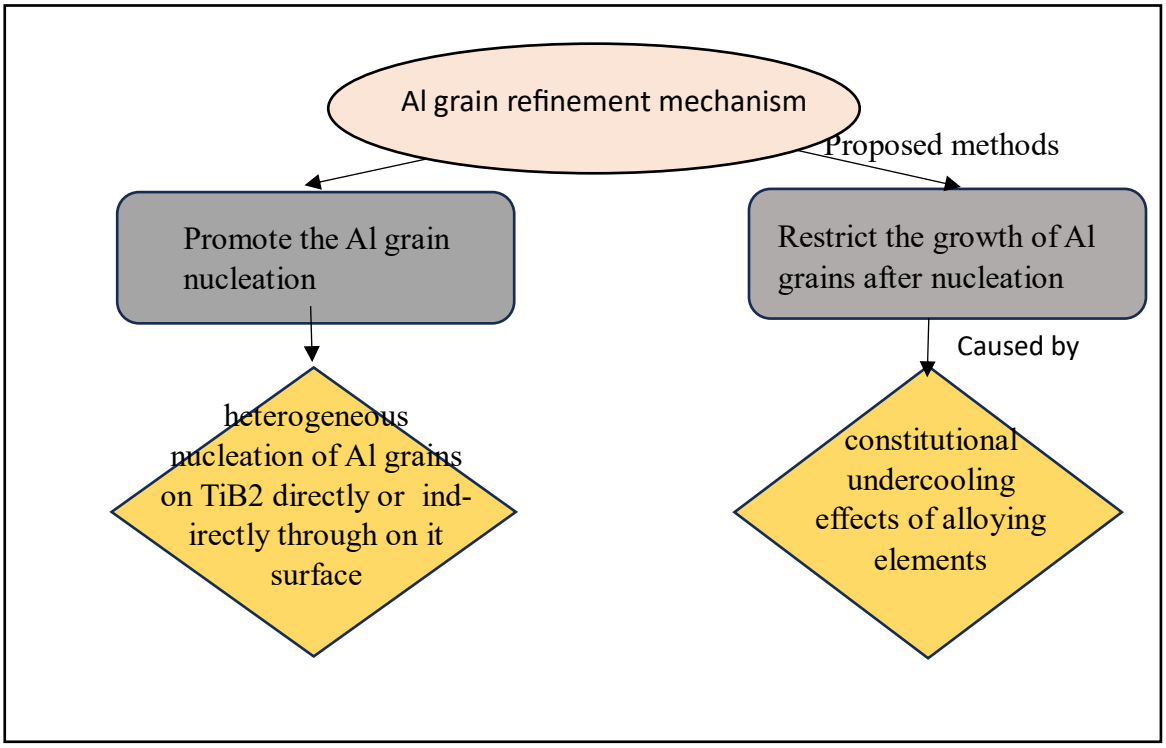
Al grain refinement mechanism
Proposed methods
Promote the Al grain nucleation
Restrict the growth of Al grains after nucleation
Caused by
heterogeneous nucleation of Al grains on TiB2 directly or ind-irectly through on it surface
constitutional undercooling effects of alloying elements

Figure 2.1: Al grain refinement proposed methods of mechanism and causes

Furthermore, it should be mentioned that the concentration of titanium in the master alloy should be kept at a level that avoids agglomeration or growth of Al_3Ti during solidification, while allowing a monoatomic dynamic layer to form along the surface of the TiB_2 particle. According to some reports, the dynamic layer may be a single atomic layer, however it will typically only be a few atoms thick. TiB_2 is not as stable as previously stated. In the presence of extra titanium and boron than the stoichiometry of TiB2, it will react with aluminium to generate a solid solution of $(Ti,Al)B_2$, which will cause titanium to continuously release into aluminium and maintain a dynamic layer of Al_3Ti. This occurs when an Al-Ti B master alloy is introduced. TiB2 facilitates the continuous release of titanium through the production of $(Ti,Al)B_2$ solid solution and the formation of an Al_3Ti layer via a coherency contact[12], [13].

2.5 Possible Reactions Occurring in Master Alloy

Possible reaction in the master alloy preparation are taken from various literature..reaction mentioned below 2.1- 2.4 are the reaction occurring in zone 1. Zone 1 is shown in Figure1.2. And are described by J.D. DONALDSON, C. P. SQUIRE in their research paper[8].

Al/K_2TiF_6:

$18K_2TiF_6 + 24Al \leftrightarrow 6(3KF \cdot AlF_3) + 18(KF \cdot AlF_3) + 18Ti$ ……..(2.1)

$K_2TiF_6 \leftrightarrow 2KF + TiF_4(g)$ …….(2.2)

Al/KBF_4:

$2KBF_4 + 2Al \leftrightarrow 2(KF \cdot AlF_3) + 2B$…… (2.3)

$KBF_4 \leftrightarrow KF + BF_3(g)$……..(2.4.)

The reaction mentioned below 2.5-2.7 takes place and produces various compound which act as grain refiners and are quoted by Nahed-El-Mahallawy[14].

$3K_2TiF_6 + 13Al \Leftrightarrow \underline{3}Al_3Ti \underline{+} 3KAlF_4 + K_3AlF_6$……(2.5)

$2KBF_4 + 6Al \Leftrightarrow \underline{4}AlB_2 + 2KAlF_4$…….(2.6)

$Al_3Ti + AlB_2 \Leftrightarrow \underline{TiB_2 + 4Al}$…….(2.7)

However, we found that reaction 2.6 proposed by Nahed-El-Mahallawy is chemically unbalanced. This reaction is further discussed in Chapter 3

2.6 Peritectic Reaction during Boride Formation(AlB_2)

The presence of AlB_2 or AlB_{12} in the Al master alloy will be eliminated if the stability of borides in the Al–B system is understood. According to X. Wang, transition metal borides have greater stability in comparison to Al borides. For the Al–Ti–B system, researchers are still unsure of the phase connection in the Al-rich corner. In order to complement the phase relationships in the Al–Ti–B system, which are crucial for the grain refinement of aluminium, X. Wang's work attempts to offer a fresh perspective on the region of the B-rich side of the Al–B phase equilibria. KBF4 reacts chemically with molten aluminium to create Al–B alloys.

Aluminium reduces boron from fluoride salt and releases it into the aluminium melt as aluminium borides, AlB_2 and AlB_{12}. The Al–B phase diagram indicates a peritectic reaction, with AlB_2 stable at ambient temperature when the boron level is less than 44.5wt.% and AlB_{12} being a high-temperature phase.

Liq Al $+AlB_{12} \rightarrow AlB_2$……..(2.8)

takes place at 975◦C. During cooling, AlB_{12} reacts with liquid aluminium to form AlB_2. However, AlB_{12} is always detected in Al–B master alloys that have been produced via

molten salt reactions at temperatures lower than the peritectic reaction temperature. The presence of AlB_{12} was also reported in Al–Ti–B master alloys that have been produced via arc melting of aluminium and boron at 800◦C. The presence of AlB_{12} at temperatures lower than 975◦C causes confusion regarding the stabilities of the boride phases in aluminium.

$$\mathbf{12KBF_4+13Al = AlB_{12}+12KAlF_4}$$

$$\mathbf{=AlB_{12}+12KF + 12AlF_3} \text{ ……..(2.9)}$$

$$\mathbf{2KBF_4+3Al = AlB_2+2KAlF_4}$$

$$\mathbf{= AlB_2+2KF + 2AlF_3} \text{ ……..(2.10)}$$

It was studied that when KBF_4 is added in to molten aluminium, it is reduced by Al and forms $KAlF_4$. It can be seen from reactions 2.9 and 2.10 that the formation of one mol AlB_{12} produces a larger quantity of $KAlF_4$ than the formation of one mol of AlB_2. Since, $KAlF_4$ is lighter in weight than aluminium and floats on to the surface of the aluminium melt. This makes the build up of boron inside the aluminium melt difficult. However, the reaction is vigorous and the build up of boron still happens. As a result the concentration of boron at the flux/melt interface may exceed 44.5wt.% locally and results in the formation of AlB_{12} at a temperature lower than 975◦C. During the reactions AlB_{12} moves into the aluminium melt away from the away from the flux/melt interface and causes a reduction in local boron concentrations. As a result the composition of the alloy moves from the AlB_2 +AlB_{12} phase region into the Al + AlB_2 phase. AlB_{12} phase is no longer stable and decomposes to form AlB_2 phase. SEM images revealed the presence of two types of phases within the boride particles: one is the AlB_2 phase represented by the large sized gray particles, whereas the other phase is AlB_{12} phase inside the AlB_2 particles represented by small dark areas inside the large particles. The engulfed AlB_{12} phase inside AlB_2 surrounded by liquid is a direct proof for the existence of a slow peritectic reaction between AlB_{12} and aluminium, which is in agreement with previous investigations on the stability of boride phases. Since the peritectic reaction,**$5Al(liquid)+AlB_{12}(solid)=6AlB_2(solid)$** occurs, the reacting solid AlB_{12} has to maintain a receding interface with AlB_2, thereby suggesting that the boron must diffuse not only within the AlB_{12} phase but also across the ever-growing AlB_2[12].

The reaction from 2.2 to 2.10 are further discussed and mass balance study was carried out to explore the potential of sludge in chapter 3.

CHAPTER 3

MASS BALANCE

In this chapter mass balance related to the production of the master alloy and its byproduct is discussed. The terms of discussion are "input material, output materials."During our study we observed that work related to mass balance during master alloy production was not reported in literature. Hence, extensively study was carried out in this chapter to explore the potential use of Sludge.

3.1Criteria for Selection of Reactions for Mass Balance

There are certain sets of reaction proposed by different researchers. One of the researcher is Donaldson who proposed below set of reactions as a result of XRD analysis of slag. They were discussed before in chapter 2.

Al/K_2TiF_6 :

$18K_2TiF_6 + 24Al \leftrightarrow 6(3KF \cdot AlF_3) + 18(KF \cdot AlF_3) + 18Ti$ ……..(2.1)

$K_2TiF_6 \leftrightarrow 2KF + TiF_4(g)$ …….(2.2)

Al/KBF_4:

$2KBF_4 + 2Al \leftrightarrow 2(KF \cdot AlF_3) + 2B$…… (2.3)

$KBF_4 \leftrightarrow KF + BF_3(g)$……..(2.4)

In the above reaction Donaldson has taken the discussion to the point where Ti and B are released into the Aluminium solution and the formation of the compounds going into the slag but has not discussed the compounds forming in the master alloy after Ti and Boron are released into the Aluminium. And hence we don't get the proportion of reactants to be feeded in the induction furnace so as to get desired amount of the master alloy. The reaction given by the Donaldson are advantageous in giving us slag composition and but are less efficient in giving us information about the master alloy composition.

So, we further carry our research to see suitable reaction giving us the information about master alloy and then we come across the reaction patented by Hancock and Davies which gives us the idea of the compounds present in the master alloy and which were quoted by Nahed El-Mahallawy et. al in their paper and are as below:

$3K_2TiF_6 + 13Al \Leftrightarrow \underline{3}Al_3Ti \underline{+} 3KAlF_4 + K_3AlF_6$……(2.5)

$2KBF_4 + 6Al \Leftrightarrow \underline{4AlB_2} + 2KAlF4$……(2.6)

$Al_3Ti + AlB_2 \Leftrightarrow \underline{TiB_2 + 4Al}$……(2..7)

Out of quoted reactions in research paper by Nahed El-Mahallawy et. al., the reaction 2.6 is unbalanced and I proposes the balanced reaction as below:

$2KBF_4 + 3Al \Leftrightarrow \underline{AlB_2} + 2KAlF4$…….(2.6.a)

So above are the possible reactions occurring during master alloy production. We will follow the reactions **2.5 ,2.7, 2.6.a** to calculate the mass balance for the master alloy preparation and also for the byproduct formation.

3.2Theoretical Considerations for Calculations of Mass Balance

To facilitate the mass balance study few following assumptions were considered.

1)Al3Ti and TiB2 and Al are the contents of TiBAl. No others borides than TiB2 are there.

2)Losses through gaseous products is considered as zero.

3) All the calculations are done for variable Ti content but the Boron content is taken as unit percent in every composition of master alloy.

3)Amount of $KAlF_4$ and K_3AlF_6 going to hood are considered in 5:1 ratio.

4)Al_3Ti remains as it is after the reaction 3.1.

As surveyed from the literature we have come across three possible reactions occurring between K_2TiF_6 , KBF_4 and Aluminium which are:

$3K_2TiF_6 + 13Al \Leftrightarrow \underline{3Al_3Ti} + 3KAlF_4 + K_3AlF_6$.....(2.5)

$2KBF_4 + 3Al \Leftrightarrow \underline{AlB_2} + 2KAlF_4$.....(2.6)

$Al_3Ti + AlB_2 \Leftrightarrow \underline{TiB_2 + 4Al}$……(2.7)

Now by concluding from the literature review we can say that Al_3Ti and TiB_2 are the compounds formed and are in the master alloy for the grain refinement. The order of above reaction is not found in the literature. But we assume its order as below on the basis of researches by the X. Wang who quoted that transition metal borides are more stable than the aluminides.

1. **$3K_2TiF_6 + 13Al \Leftrightarrow \underline{3Al_3Ti} + 3KAlF_4 + K_3AlF_6$**
2. **$2KBF_4 + 3Al \Leftrightarrow \underline{AlB_2} + 2KAlF_4$**

3. $Al_3Ti+AlB_2 \Leftrightarrow \underline{TiB_2 +4Al}$

Now, by adding reaction 1 to 2, we get reaction 3.1 then there is reaction between the products of reaction 3.1. The reaction between products Al_3Ti and AlB_2 results in the formation of TiB_2 and Aluminium and excess Al_3Ti remains as it is.

$$3K_2TiF_6 + 13Al \Leftrightarrow \underline{3Al_3Ti} + 3KAlF4 + K_3AlF_6$$

$$+ \quad 2KBF_4 + 3Al \Leftrightarrow \underline{AlB_2} + \textit{2KAlF4}$$

$$3K_2TiF_6 + 16Al + 2KBF_4 \Leftrightarrow \underline{3Al_3Ti + AlB_2} + 5KAlF_4 + K_3AlF_6 \ldots..(3.1)$$

$$\Updownarrow$$

$$\underline{TiB_2 + 2Al_3Ti + 4Al}$$

The products underlined in the final reaction which are Al_3Ti, Al, TiB_2 forms master alloy and rest is Slag or PAF.

Now we come to calculation part, we take the chemical composition of the formed master alloy. For which we take approximate values of the atomic weight of the elements as: Potassium (K)=39 g/mol, Titanium (Ti)=48 g/mol, Fluorine (F)=19 g/mol, Boron (B)=10 g/mol,Aluminium (Al)=27;

Accordingly, value of the molecular weight of the compounds comes out to be:

K_2TiF_6 =240 g/mol, KBF_4= 126 g/mol, Al_3Ti=129 g/mol, TiB_2=70 g/mol, $KAlF_4$=142 g/mol, K_3AlF_6 = 258 g/mol.

Now if we take out the chemical composition in terms of atomic weight % of **(2**Al_3Ti+ **4Al+**TiB_2**)** then we get it as Al-33Ti-5B. So as to make the composition Al-3Ti-1B we need to add here more amount of pure Aluminium. We go increasing the moles of Aluminium input on the reactant side of the reaction (3.1) from 16 to 154 moles. And we get the composition Al-3Ti-B. The stoichiometrically satisfied reaction of desired composition is as follows:

$$3K_2TiF_6 + 2\ KBF_4 + 154\ Al \Leftrightarrow \underline{2\ Al_3Ti + TiB_2 + 142Al} + 5\ KAlF_4 + K_3AlF_6 \ldots.(3.1.a)$$

Now whole PAF is not lost in forming sludge since it is periodically removed from above master alloy layer through hopper till the surface of master alloy is seen. Only few % of PAF produced enters hood to react with NaOH to form the sludge.

Now we have to make sludge 1kg in weight which implies weight of the product should be equal to 1 kg. NaOH solution is made to react with PAF so here we assume alkali bases go away with water after the process of filtration and remains there the water insoluble Cryolite, Elapsolite, Potassium Fluoride, Aluminium trifluoride and some unreacted PAF as a filtrate. Above discussion implies that,

(½ Na_3AlF_6+ ½ K_2NaAlF_6 +5KF + 5AlF_3) should weigh 1000 g

(½ Na_3AlF_6+ ½ K_2NaAlF_6 +5KF + 5AlF_3)=Sludge

PAF ⟶ Sludge

(5 $KAlF_4$ + K_3AlF_6) weighs 968 g.

(½ Na_3AlF_6+ ½ K_2NaAlF_6 +5KF + 5AlF_3) weighs 936 g

Therefore, % loss in weight while conversion of PAF to Sludge =[{(weight of (5 $KAlF_4$ + K_3AlF_6)) - (weight of Sludge formed in reaction 3.5)}/(weight of (5 $KAlF_4$ +K_3AlF_6))] *100

= ((968-936)/968)*100

=3.31

Now to get amount of PAF (in g) that should go to hood to form 1000g/1kg sludge is given by

=1000+1000*3.305% = 1000+33.05 = 1033.1g

(½ Na_3AlF_6+ ½ K_2NaAlF_6 +5KF + 5AlF_3) should weigh 1000 g

But a/c to recation 3.5 (½ Na_3AlF_6+ ½ K_2NaAlF_6 +5KF + 5AlF_3) weighs 936 g.

Let (½ Na_3AlF_6+ ½ K_2NaAlF_6 +5KF + 5AlF_3)= ‘s’

Let the factor to be multiplied to ‘s’ be ‘f’ so that ‘s’ weighs 1000 g.

Thus by using theorem of Ratio and Proportionality,

$s = 936$

$s_1 = 1000$

$s/s_1 = 936/1000$

$f = 1000/936$……..(s_1/s)

=1.07

Multiplying the (½ Na_3AlF_6+ ½ K_2NaAlF_6 +5KF + 5AlF_3)= ‘s’ by 1.07

We get,

0.535 Na_3AlF_6+ 0.535 K_2NaAlF_6 +5.35 KF + 5.35 AlF_3= 1000 g

Now % PAF going to hood =(1033.1/232580.49)×100

=0.444%

Therefore, due to 0.444% loss of PAF 1 kg of Sludge is forming.

3.3 Effect of Composition of Master Alloy on the Amount Of PAF-Sludge Production

In this section effect of the composition of master alloy on the amount of PAF-Sludge was discussed. From the above mass balance calculations, various graphs were plotted, and discussions were made thereon. The theoretical data obtained from the mass balance calculations were related to the actual industrial observations. The conclusions were drawn, which are discussed in subsequent sections.

The graphs were plotted by using the following relations-

$$\% \text{ master alloy production} = \left[\frac{\text{Weight of master alloy produced}}{\text{Weight of total input material}}\right] \times 100$$

$$\text{Similarly,\% PAF produced} = \left[\frac{\text{Weight of PAF produced}}{\text{Weight of total input material}}\right] \times 100$$

$$\text{also, \% Sludge produced} = \left[\frac{\text{Weight of Sludge produced}}{\text{Weight of total input material}}\right]$$

3.3.1 Graphical representation of % of various outputs with respect to input material

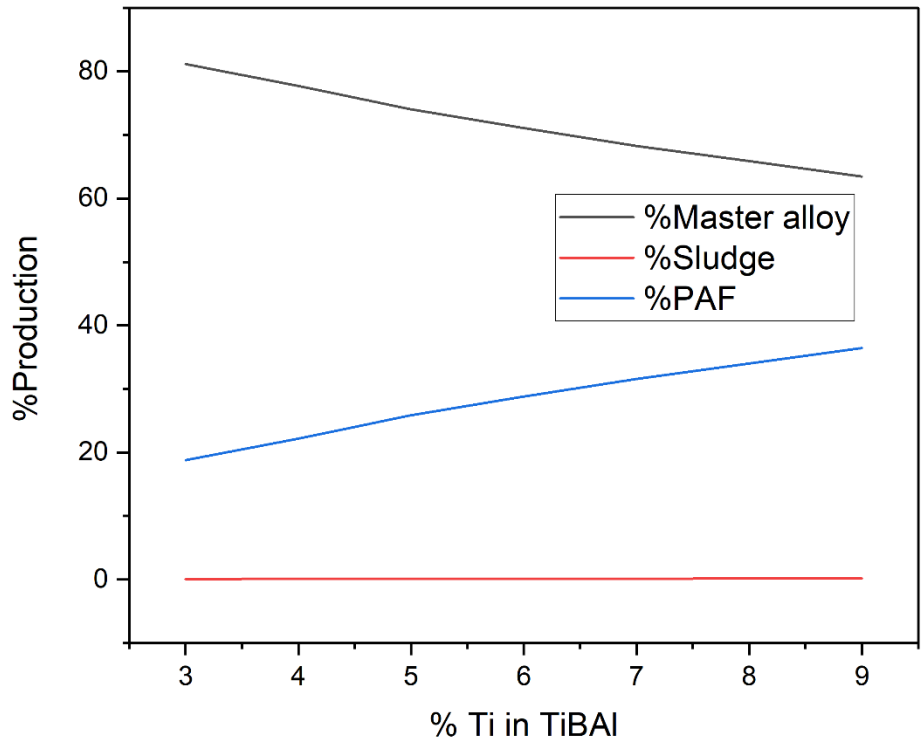

Figure 3.1 Graphical representation of % of various outputs with respect to input during master alloy production

For the above calculations few assumptions were made which are quite in tune with the actual industrial practice. These parameters/conditions are as follows-

1) %loss of PAF in the hood during the production of different compositions of master alloy is the same.

2) Keeping the furnace conditions, like temperature, are assumed to be constant during the production of different compositions of TiBAl.

By varying the amount of the w/w%Ti, the graph is plotted and presented in the figure no 3.1. From the graph, we can observe that the amount of master alloy formed decreases and the amount of PAF produced increases as the w/w 5 of TI increases. subsequently amount of sludge produced also increases.

PAF production increases as a result of an increase in addition of halide salts K_2TIF_6 and KBF_4, which are added to increase the amount of Ti in the master alloy.

3.3.2 Graphical representation of the possible % compounds in TiBAl master alloy different composition

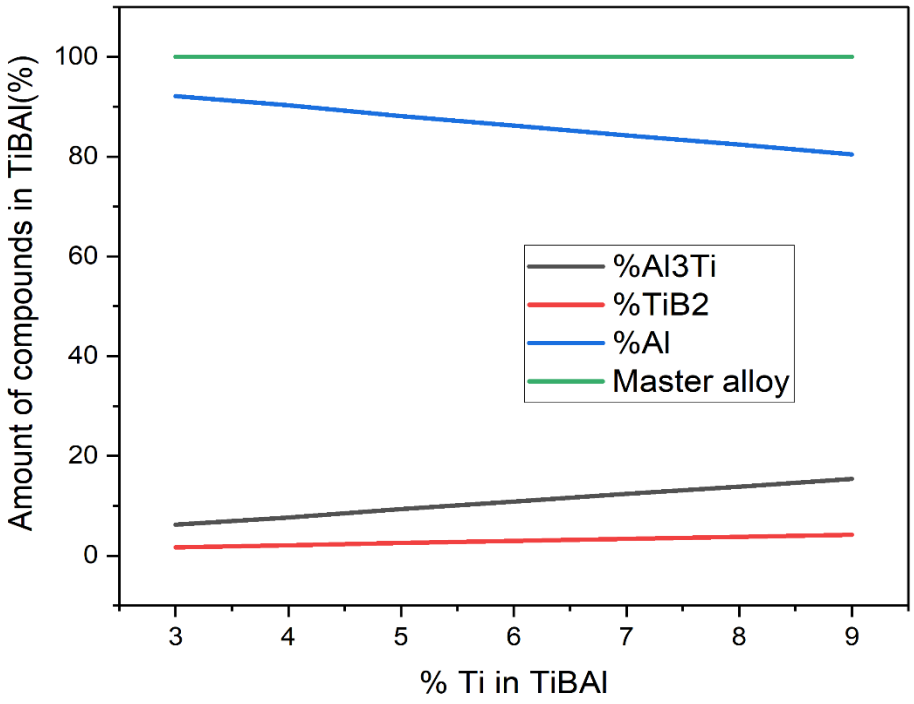

Figure 3.2 Graphical representation of the possible % compounds produced during production in TiBAl

For the above calculations few conclusions are drw=awn which are discussed below:

1) As the amount of Ti goes on increasing in master alloy the amount of TiB_2, Al_3Ti goes on increasing.

Wang and Han stated "The concentration of titanium must be maintained to a level that is high enough to form a dynamic layer of Al_3Ti in solidification and low enough to avoid the agglomeration or growth of Al_3Ti. The dynamic layer by nature will be only a couple of atoms thick, with a possibility of being a single atomic layer as reported by others. TiB_2 is not as stable as reported before. It will react with aluminum to form (Ti,Al)B2 solid solution leading to the constant release of titanium into aluminum to maintain a dynamic layer of Al_3Ti in the presence of excess titanium and boron than the stoichiometry of TiB_2 when an Al-Ti B master alloy is added." Above statements and my graphical representation can be complementary to each other as the graph clearly shows amount of Al_3Ti > amount of TiB_2. Since there is thin

layer of Al_3Ti around the TiB_2 and the thin layer may be monoatom layer thin. Or this graph can be second proof of the theory above.

3.3.3 % Input raw material required for production of master alloy of different composition

For the calculation, we considered the production of 1000 kg master alloy as the basis. For various types of TiBAl, varying from 3% Ti to 9% Ti by weight, the amount of halide salts were calculated and graph was plotted in figure no 3.3. It shows that with increase in Ti% amount of salt required increases and the amount of Al addition decreases.

We can observe that the amount of K_2TiF_6 addition increases along with the KBF_4 addition, which leads to an increase in the formation of TiB_2.

The findings are in tune with the observations reported by various researchers.

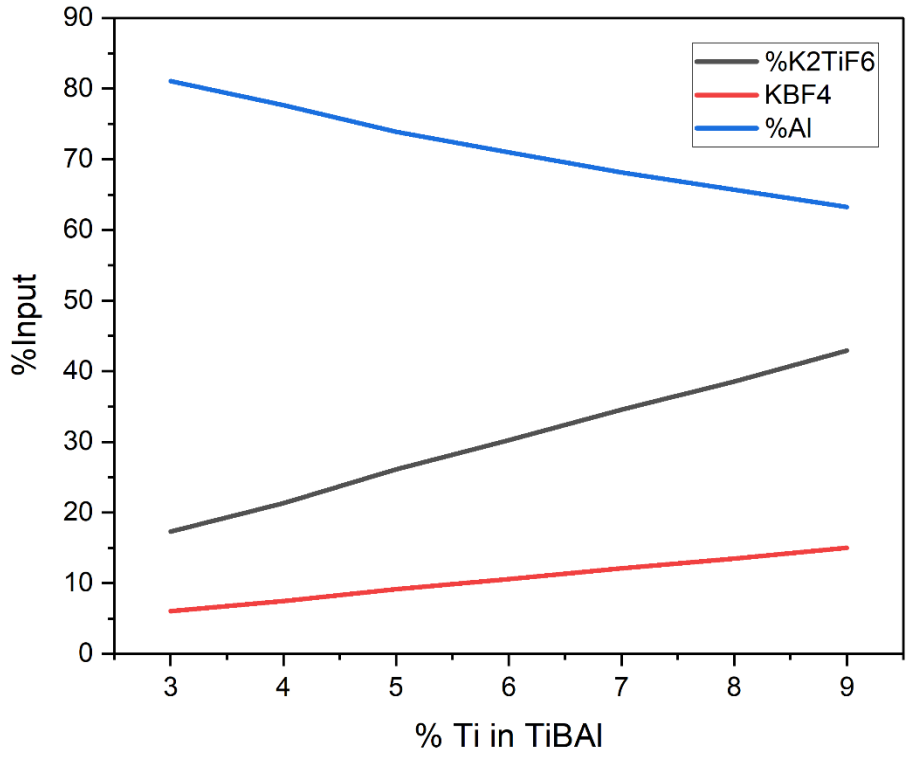

Figure 3.3 Raw material required for production of master alloy of different

3.4 DISTRIBUTION OF ELEMENTS IN THE SYSTEM

To trace the route of the elements travelling in the present system following calculations were done and the model was proposed in figure no 3.4, 3.5, 3.6 and 3.7

For the calculations, the Al-3Ti-B master alloy was considered.

3.4.1 Distribution of Fluorine

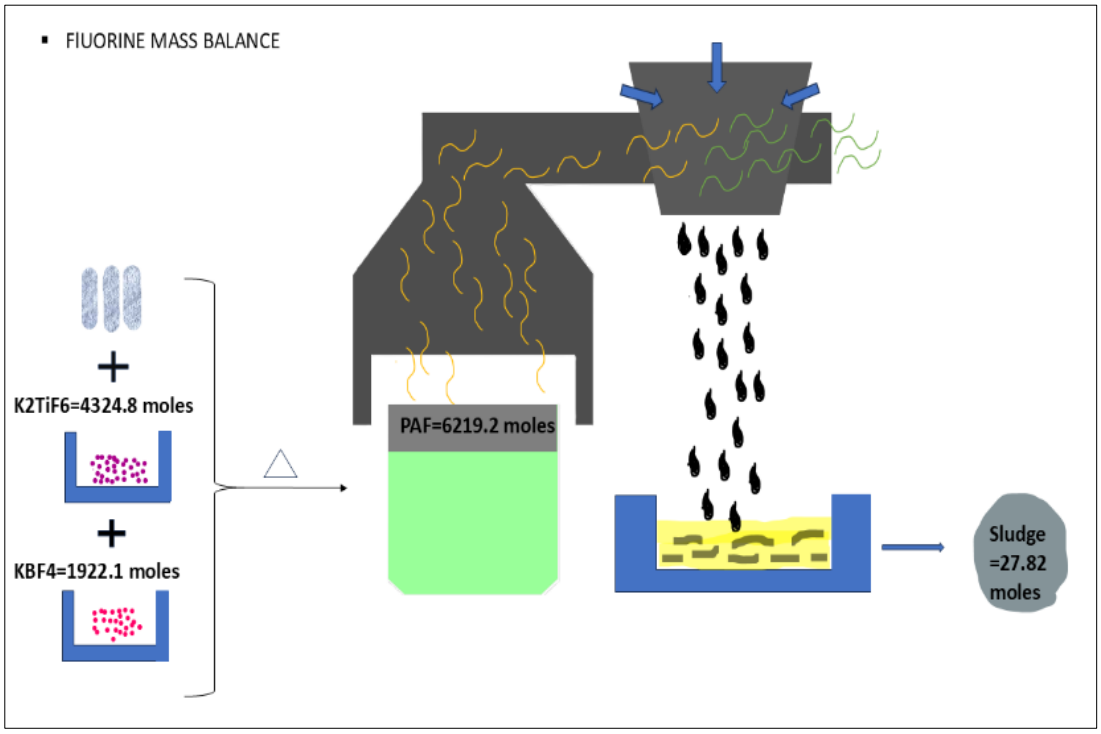

Figure 3.4 Mass Balance for Fluorine for Al-3Ti-B master alloy

Here, through K_2TiF_6 4324.8 moles of Fluorine are put into the process while through the KBF_4 1922.1 moles of Fluorine are put into the process.

All of the Fluorine put in the process goes to the PAF and then to sludge. PAF contains 6219.2 moles of Fluorine And sludge contains 27.82 moles of Fluorine.

Input amount of Fluorine = Output amount of Fluorine

$(nK_2TiF_6 \times 6) + (nKBF_4 \times 4) = (nKAlF4 \times 4) + (nK_3AlF_6 \times 6) + (nSludge)$…n= no of moles

4324.8 +1922.1 = 4805.4 + 1441.6 +27.82

Thus, we get Input Fluorine= Output Fluorine

3.4.2 Distribution of Potassium

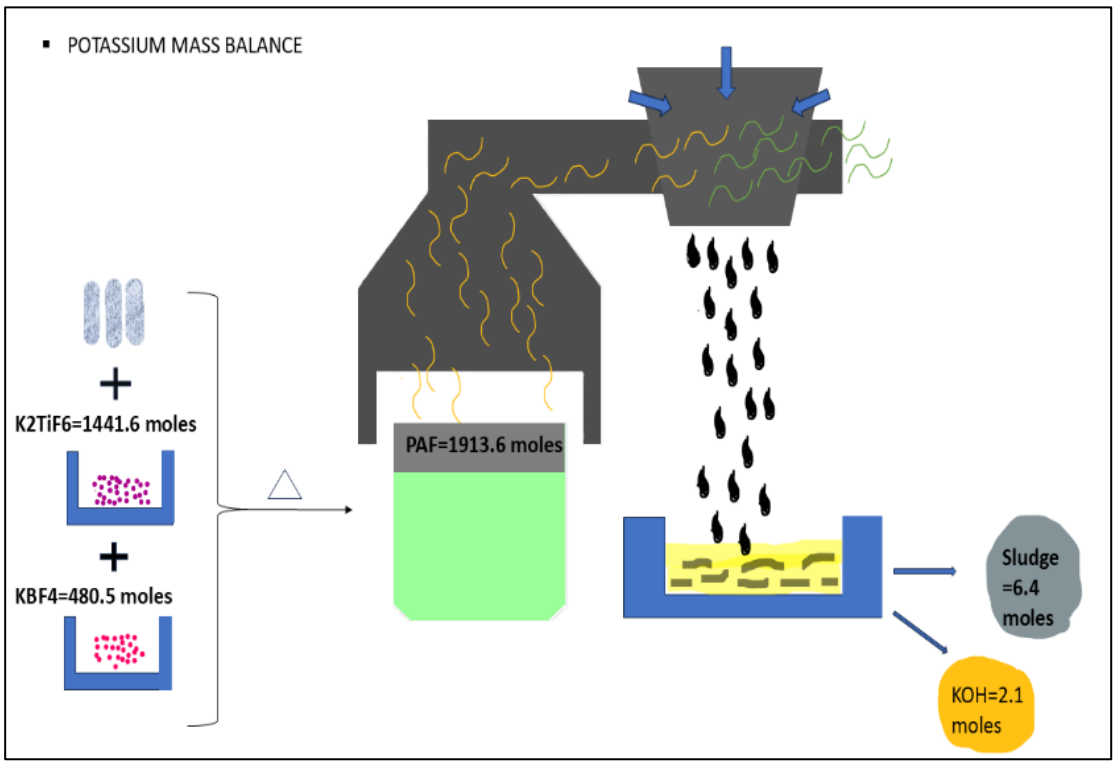

Figure 3.5 Mass Balance for Potassium for Al-3Ti-1B master alloy

In the process Potassium input through K_2TiF_6 is 1441.6 moles while from KBF_4 is 480.5 moles.

No potassium is going in master alloy. All the potassium joins the PAF and sludge. Moles of Potassium in PAF are 1913.6 and in the sludge is 6.4 moles while Potassium joining hydroxide ions to form KOH is 2.1 moles.

$(nK_2TiF_6 \times 2) + (nKBF_4 \times 1) = (nKAlF4 \times 1) + (nK_3AlF_6 \times 3) + (nSludge)$

1441.6 + 480.5 =1913.6 + 2.1 + 6.4

Therefore, input amount of K= Output amount of K

3.4.3 Distribution of Aluminium

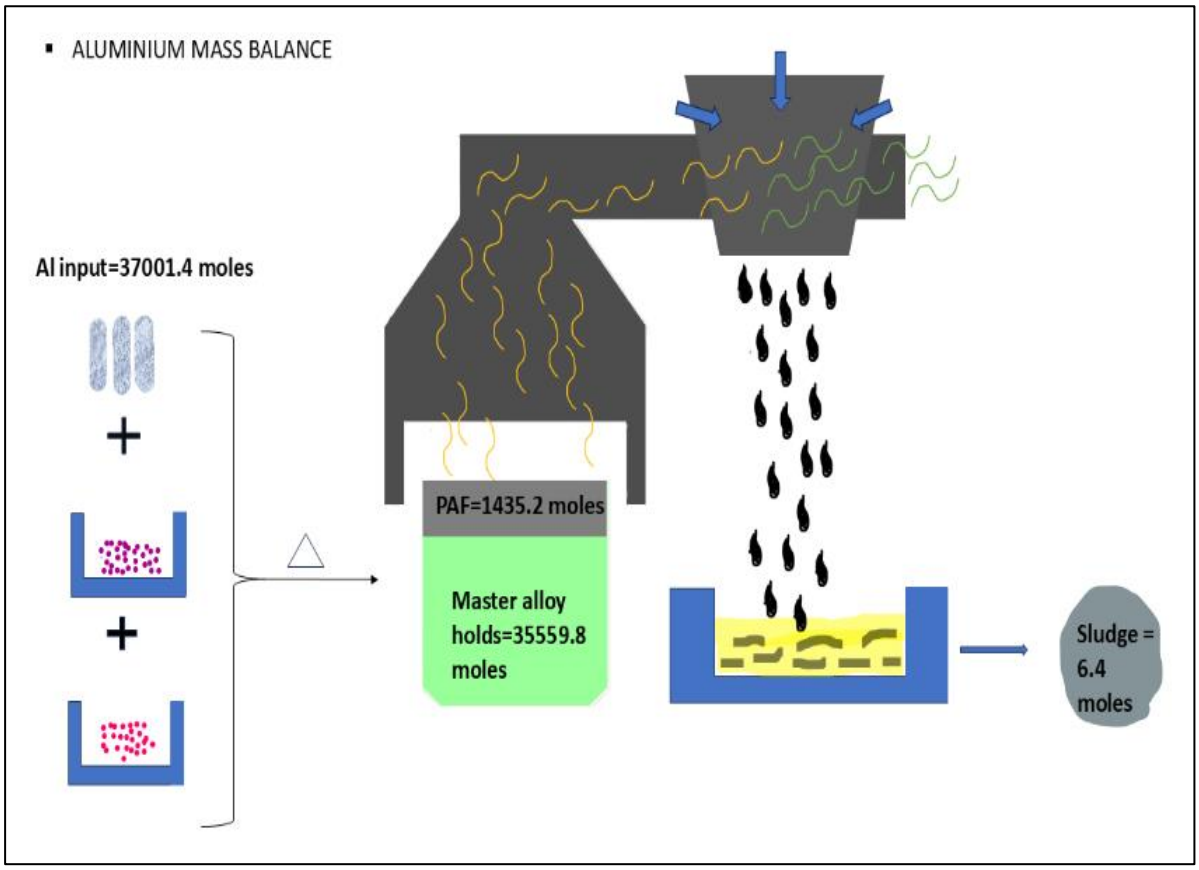

Figure 3.6 Mass Balance for Aluminium for Al-3Ti-B master alloy

Aluminium input in the process is through the Al ingot. So, for preparation of 1000000 g Al-3Ti-B master alloy, input Al moles is 37001.4. Al goes to master alloy ,PAF, and to sludge. Master alloy holds 35559.8 moles of Al ,PAF holds 1435.2 moles and the Sludge holds 6.4 moles.

n_{Al} input = n_{Al} in M.A.+ n_{Al} inPAF +n_{Al} in Sludge

37001.4 moles = 35559.8 +1435.2 + 6.4

Input amount Al = Output amount Al

3.4.3 Distribution of Sodium

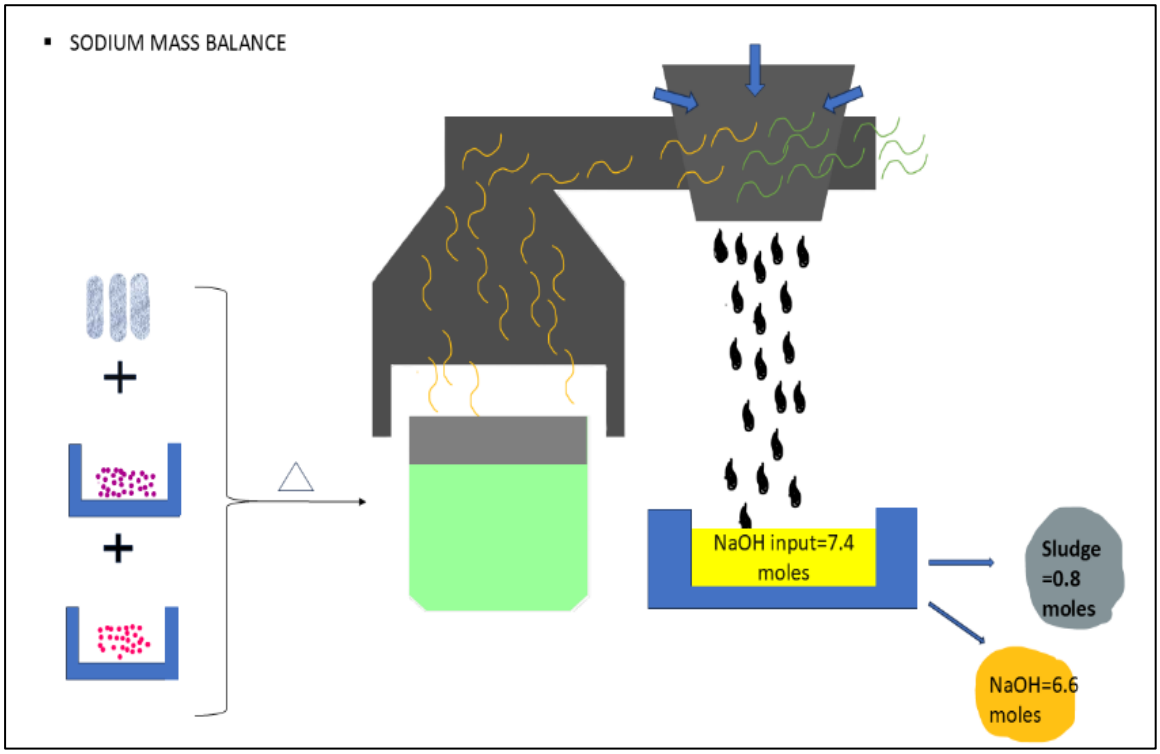

Figure 3.7 Mass Balance for Sodium for Al-3Ti-B master alloy

Sodium enters into the system at the last stage of process through NaOH pool. Now, we have dopped the NaOH where 7.4 moles of sodium are there 7.4 moles of NaOH is there. So out of these 7.4 moles of Na 6.6 moles go with water as NaOH which is alkali base. And rest go with the sludge.

n_{NaOH} input = n_{Na} in water + n_{Na} in Sludge

7.4 moles = 6.6 moles + 0.8 moles

Input amount of Na = Output amount of Na

Similarly, mass balance for different composition of the master alloy was also calculated.

3.5 Composition of Sludge as Calculated from Mass Balance

After getting mass balance of all the elements the composition of the sludge was calculated on the basis of the mass balance proposed.

Table 3.1 Composition of sludge on the basis of mass balance

Elements	F	K	Al	Na
%predicted in sludge	52.8	25.0	17.3	4.9

These theoretical calculations are further discussed with the practical studies in Chapter 5.

CHAPTER 4

EXPERIMENTAL METHOD

To characterise the Sludge various techniques used are discussed in this chapter. The Sludge was characterised using SEM, XRD, XRF etc. Thus, in this chapter 4 details about the characterisation of the sludge are discussed. In this chapter attempts are discussed that are made to determine the solubility of the Sludge in the different solvents. Also attempts and methodology to make composites are discussed.

4.1 Characterisation of the Dry Sludge using SEM, XRD, XRF, etc.

The Dry Sludge was collected from Minex Metallurgical Company, ltd, Nimji. The sludge we are getting as a waste product during Aluminium master alloy production was characterised using various techniques such as SEM, XRD and WD-XRF. Sludge was tried to observe under optical microscope so that its particle size could be determined. Due to the very fine size of the Sludge particles which was beyond the resolution limit of the optical microscope, the particle size could not be revealed. So, SEM done after optical microscope for particle size determination and for knowing the morphology. Ethanol was tried to use for reducing the agglomeration so as to get the clarification about particle shape and size . Sludge was dissolved in Ethanol and then placed on sample holder of SEM machine. Platinum coating was done of the sample. After coating sample was observed in SEM machine of company JEOL. Later WD-XRF was done using Thermo SCIENTIFIC XRF model ARL- PERFORM`X machine in Sunflag Iron and Steel Company Limited. For compound determination XRD was done using X-Ray diffractometer smart lab SE 3KW in Department of Physics, VNIT. Special efforts have been taken to know the chemical compositions of the sludge. Preliminary studies like solubility, acidity-basicity test were done. When sludge was dissolved in water it is acidic or basic was found out by litmus paper and its pH was tested by pH metre by using the Electronics India Digital pH meter Model-111. Combustion test was performed by holding sludge on spatula on a bunsen burner for 10 min.

4.2 Solubility of Dry Sludge in different Solvents

Solubility of the Sludge was tested in different media such as inorganic acids like HCl, H_2SO_4, HNO_3 etc. 10% solution of each was prepared and was kept as it is for some time

so as to give time to the reaction to occur and then was filtered using Whatman filter paper. Loss in weight were taken. This attempt was made so as to check how much amount of Sludge gets dissolved in the solvents. Also solubility of the Sludge in organic solvents like DMSO and THF was checked. The sludge was mixed with water and then was slightly heated and stirred for some time. Then it was filtered using Whatman Filter paper. The analysis of the filtrate was done in the Becquerel Lab Pvt Ltd, Butibori to see how much amount of Fluoride, Sodium, and Potassium ions goes into water after dissolving it into the water. 10 g of sludge was dissolved in 100 ml of water for this test i.e 10% solution of sludge in water was taken.

4.3 Effect of Temperature on Sludge

To study effect of temperature on sludge, i.e. to check whether the new compound is formed or not in it by fusion of old compounds or to check the temperature bearing capacity of the sludge, it was heated to 1000ºC. It was also heated to see whether there would be any change in morphology, colour of the sludge or not after heating it. It was heated to 1000ºC for 2 hours in Das and Company tubular furnace in Chemical Analysis Lab in Department of MME, VNIT. Afterwards, SEM and XRD of the sample heated to 1000ºC were done. Also loss in weight was noted.

4.4 Study on Bakelite-Sludge Composite

An attempt was made to mount the sludge on the hot mounting machine. Hot mounting machine was of company METCO. The dry sludge sample was put in between the Bakelite powder in the Bainmount Twin H auto Specimen mounting press. It was placed in the machine the temperature reached around 140ºC and pressure around 1 barr. The mounting process ran for around 15 min. Then the sample was allowed to cool down for some time inside the machine itself.

4.5 Study on Al-Sludge Composite

An attempt was made to form the composite out by mixing dry sludge after heat treatment upto 1000ºC, with the commercial Aluminium. The ample amount of sludge was taken and was heat treated to 1000ºC in the furnace. Later it was air cooled. Then was taken to Star Industries where aluminium was melted and poured in the mould and while pouring the molten metal slowly Sludge powder was also put into the mould .

Three samples were casted. First sample contained only commercial Aluminium with 0% sludge addition weighing approximately 200 gm. In the second mould 20 g of Sludge was mixed with approximately 200 gm of the Aluminium melt. Thus, the amount of Sludge added to the Aluminium is 10%. In the third mould 25 g of Sludge was mixed with approximately 200 g of the Aluminium. Hence, the amount of Sludge added to Aluminium is 12.5%. In above case we assume that all of Sludge added in the melt was absorbed by the Aluminium. Later, the castings were allowed to cool and the sample pieces were cut down from the moulding for testing. Characterisation of the sample was done using SEM, EDS. Its morphology was studied using SEM. Grain structure was observed using the optical microscope.

For microstructural studies it was polished on emery paper up to grade of 2500 grit and then was cloth polished using the silvo-paste and then was etched for about 3 seconds using Kellers's reagent. Thus, the microstructure revealed were studied. Difference between the three was analysed.

For hardness, Micro-Vickers Hardness test was done on three samples. The load of 0.1 HV was applied and three reading on a sample were taken. Average of three readings was considered as the hardness value of the sample.

The density of samples was calculated using the Digital Density Meter. Mean of two readings taken was taken as the density of the sample.

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CHAPTER 5
RESULTS AND DISCUSSION

This chapter is devoted to discuss the results of the test and experiments conducted during this investigation. The results are thoroughly discussed discussed to get the comprehensive understanding of the dataset and potential use of Sludge.

5.1 Results of Characterisation of the Dry Sludge using SEM, XRD, XRF, etc.

5.1.1 Preliminary observations:

The appearance of dry sludge is grey. But when it comes in contact with the water it appears black in colour. Its texture is like chalk powder or talc powder. Combustion test was done by holding the dry sludge in spatula on Bunsen burner for 10 min and it was observed that the dry sludge is incombustible. A 10 % solution of the dry sludge in water was made. The pH meter was calibrated using the buffer solutions of pH 4 and 7. And then the reading of pH meter was noted down which came out to be 3. The pH of the 10% solution of the sludge was acidic.

Figure 5.1 Dry Sludge as received from industry

5.1.2 Observations using SEM:

It was observed under the scanning electron microscopy. Its morphology was observed to be mixture of cubic and cuboidal its particle size is between 300-500 nm.This observations are in tune with the literature and indicate the presence of AlF_3 from the morphology of Sludge[19]. The exact particle size could not be determined since agglomeration was there. So, range of partice size is determined.

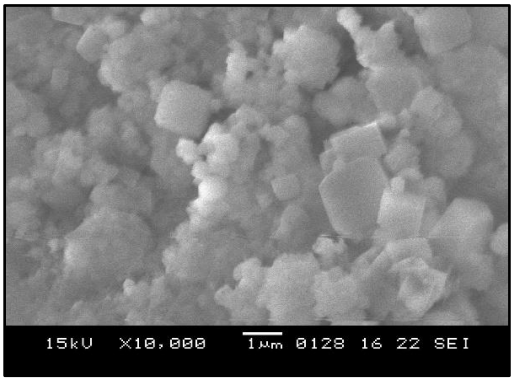

Figure. 5.2.a SEM image of Sludge

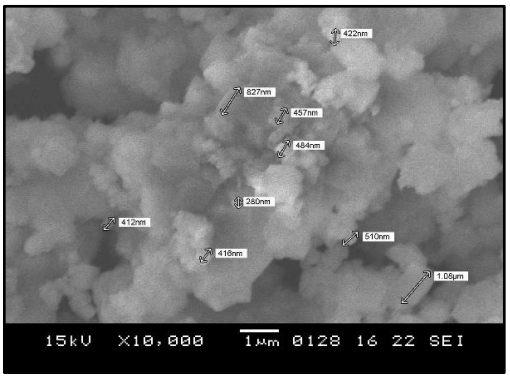

Figure 5.2.b Particle size determination of Sludge

The SEM images of Sludge dissolved in ethanol is shown. We can observe that the agglomeration is not removed. The results are unsatisfactory.

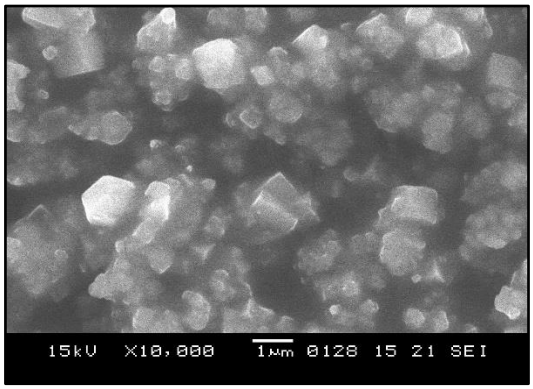

Figure. 5.3.a . SEM image of sludge after treating with ethanol

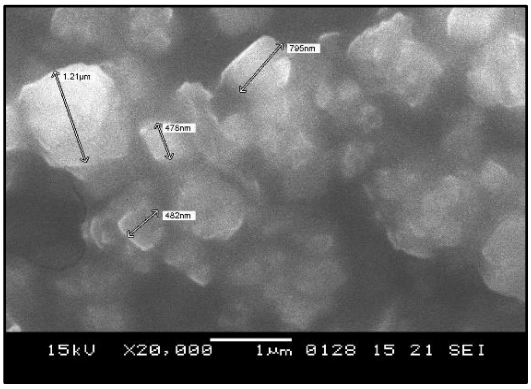

Figure 5.3.b Particle size determination of sludge after treating with ethanol

5.1.3 WD-XRF studies of the Dry Sludge

The speciality of the fluoride and oxide containing sludge is that fluorides and oxides are hard to be detected by XRF machines due to the less characteristic production of the X-ray by the fluorides and oxides. Highly sensitive XRF machines are required. Here we can see that the estimated error of the detected compound is highest for the element with the lowest atomic number. The chemical composition of sludge is given below in Table 5.1.

Table 5.1 WD-XRF results of the dry sludge

Elements Present	Fluorine (F)	Sodium (Na)	Potassium (K)	Aluminium (Al)	(Ba+ Ca+ Mg+…. +Si)
Actual wt%	46.92	20.37	17.10	11.49	<5
Estimated error	0.25	0.2	0.19	0.16	<0.2
Predicted wt %	52.8	4.9	25	17.3	-
Error between actual and predicted	5.88	-15.47	7.9	5.81	-

Here it is observed that the elements Fluorine, Aluminium and Potassium are present in theoretical sludge in amount 6-7% more than that of the practical composition. . Sodium is going out of trend by showing presence of about 15% lesser in actual sludge than theoretical sludge. The reason behind this is that : The NaOH we are putting in the mass balance is stoichiometrically determined but in actual practice the amount of NaOH incorporated may be higher than the stoichiometry values of reaction 3.5 from section 3.2.

5.1.4 Detection of compounds using XRD

XRD was done, which was analysed using the Xpert Highscore Plus and indexed using Origin 2025. The very first thing that can be concluded by observing XRD graph is that the material is highly crystalline because peaks are very sharp. We can study the dissociation of $KAlF_4$ and K_3AlF_6 at higher temperature and also can find the presence of new compounds through the XRD. Thus the phases that are found in the XRD graph of the untreated dry sludge are K2NaAlF6 and Na3AlF6 and SiO2[20]. The standard colour of compound Elapsolite is grey. The colour of the sludge is grey that may be because of the dominancy of presence of Potassium Sodium Aluminium Fluoride.

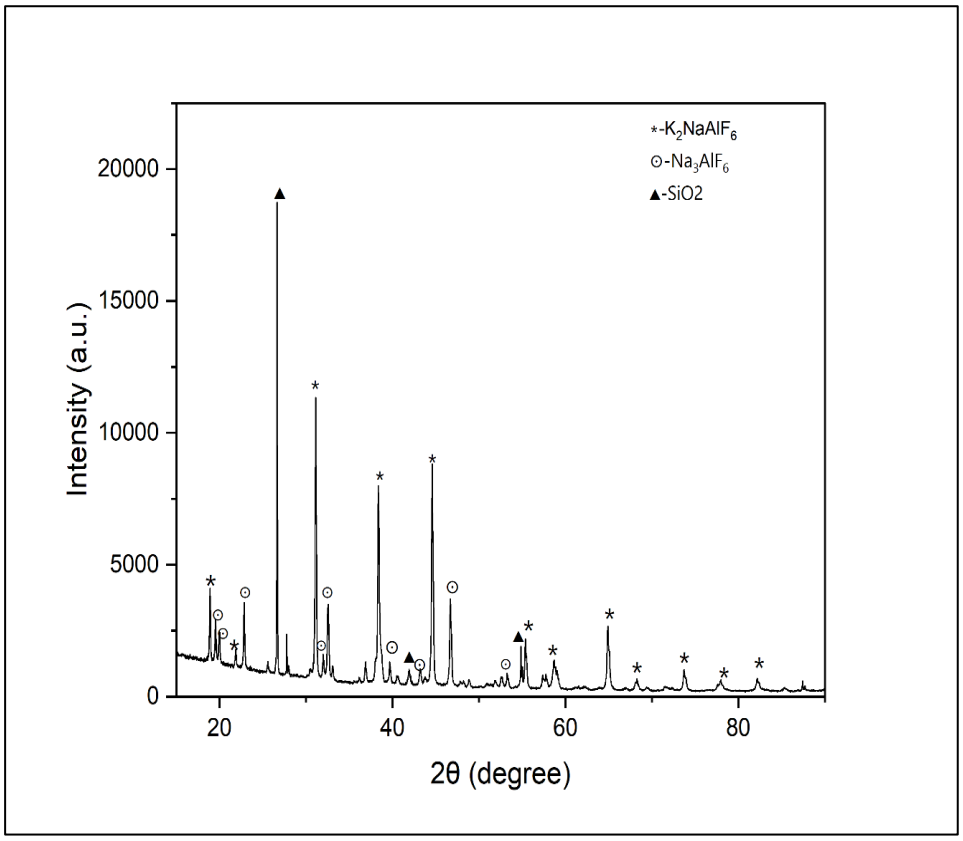

Figure 5.4 XRD graph of the Dry SLudge

5.2 Solubility of Dry Sludge in different Solvents

Attempt was made to know the solvent in which sludge is soluble. So various solvents like the H_2SO_4, HNO_3, HCl, H_2O, DMSO, THF were tried. There may be the possibility of replacement of oxygen from above solvents by Fluorine[21]. Beside this sludge was also dissolved in universal solvent i.e. water. No change in colour of solvents was observed after dry sludge was put into it. Also, weight loss found after filtering and measuring the weight of the residue very less change in weight was found.

Molecular structure of the solvents are as follows:

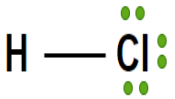

Figure 5.5.a Structure of HCl

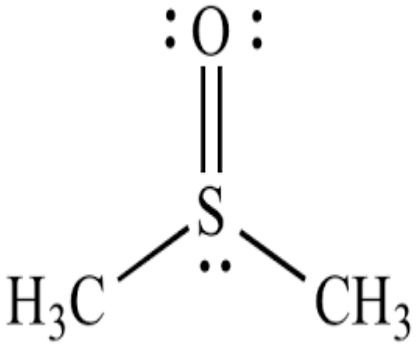

Figure 5.5. b Structure of DMSO

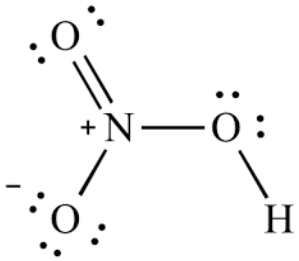

Figure 5.5.c Structure of Nitric acid

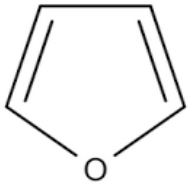

Figure 5.5.d Structure of THF

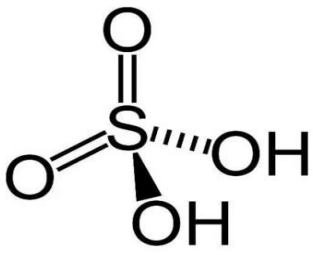

Figure 5.5.e Structure of Sulphuric acid

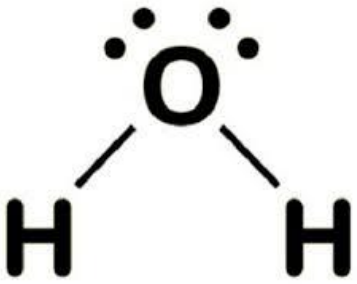

Figure 5.5.e Structure of Water

Sludge was mixed with water to study the effect of dissolution of sludge in water. And the results are from 10% solution of the sludge the amount of Sodium, Fluorine, Potassium, Boron that leached into the water are as enlisted in the table 5.2.

Both sodium and potassium leached into the water at high concentrations, indicating that their compounds in your sample are highly soluble and readily mobilized when in contact with water. This behavior is typical for many sodium and potassium salts[22].

Despite the high fluorine content in the sample, only a small amount of fluoride (2.98 mg/L) leached into the water. This suggests that most fluorine in sample is present in forms that are not highly water-soluble, or that the leaching conditions (such as pH, presence of competing ions) limited fluoride release[23], [24], [25], [26], [27], [28].

Studies show that higher sodium levels and alkaline conditions can promote fluoride leaching from minerals, but in this case even with high sodium, fluoride release remained low, reinforcing that the fluorine is likely bound in less soluble forms. The pH of the filtrate came out to be 4.45 which is acidic. And hence we can say that acid is prepared out of the Sludge.

Table 5.2 Effect of sludge when mixed in water

Element	Result (mg/L)
Sodium (as Na)	412.40 mg/L
Potassium (as K)	401.20 mg/L
Boron (as B)	79.37 mg/L
Fluoride (as F)	2.98 mg/L

Reactions of PAF with H_2SO_4:

1)$KAlF_4(s) + 2\ H_2SO_4(aq) \rightarrow 3Al_2(SO_4)_3(aq) + 2\ KF(aq) + 6\ HF(g)$…5.1

2)$K_3AlF_6 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6HF + 3K_2SO_4$ …….5.2

Reactions of PAF with HCl:

$KAlF_4$ (s) + 4HCl (aq)→ KCl (aq) + $AlCl_3$ (aq) + 2HF (aq)……..…..5.3

$K_3AlF_6(s)+6HCl(aq)\rightarrow 3KCl(aq)+AlCl_3(aq)+6HF(aq)$…….5.4

Reactions of PAF with the HNO3:

$KAlF_4(s) + 4HNO_3(aq) \rightarrow 4HF(aq) + KNO_3(aq) + Al(NO_3)_3(aq)$…….5.5

$3AlF_6 + 3HNO_3 \rightarrow 3KNO_3 + Al(NO_3)_3 + 3HF.$ …….6.6

Table 5.3 Effect of sludge mixed in different solvents

Solvent	Initial weight of sludge (g)	Final Weight of Sludge(g)	% reduction in weight
HCl	3.0205	2.5680	14.99
HNO_3	3.2044	2.6660	11.85
H_2SO_4	3.1008	2.725	12.125
DMSO	3.051	2.9330	3.866
THF	3.108	2.993	3.698
H_2O	3.0109	2.8604	4.998

From the table we can state order of solubility of the Sludge in solvents is as: HCl > H2SO4 > HNO3 > H2O > DMSO > THF

Inorganic solvents has dissolved the Sludge more than organic solvents.

5.3 Effect of Temperature on Sludge

Figure 5.6.a Dry sludge in boat shaped crucible before heat treatment

Figure 5.6.b Dry sludge in furnace at 1000ºC

Figure 5.6.c Dry sludge in crucible after heat treatment

After heating the colour change was observed form grey to white and fusion in between particles was observed. It was weighed and loss in weight was noticed.

1. Initial weight of sludge: 1.0073 g
2. Final weight of sludge : 0.9158 g

3. LOI of sludge :9.08%

5.3.1 SEM images

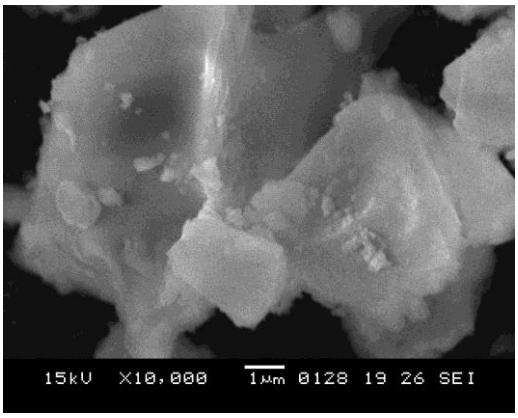

Figure 5.7.a SEM image of the preheated dry Sludge to 1000ºC

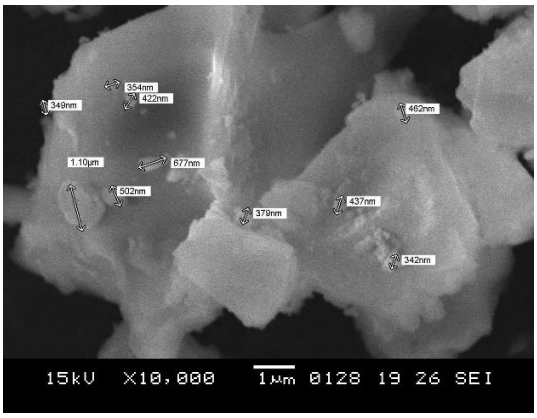

Figure 5.7.b. SEM image of the preheated dry Sludge to 1000ºC indicating particle size

The colour of preheated powder to 1000 degree celcius is white and has some red colured granules.EDS of the dry sludge which was preheated to 1000º C was also done. It shows the presence of Fluorine, sodium , Aluminium , Oxygen, Potassium elements. The semi-quantitative wt% are tabulated in table no. 5.4

Table 5.4 EDS results of the preheated dry sludge to 1000ºC

	F	**Na**	**K**	**Al**	**O**	**Others**
Normalized wt%	26.11	19.73	7.19	9.97	24.11	<11
Error wt%	3.59	1.42	0.28	0.56	3.32	<0.83

5.3.1 XRD study :

XRD graph was analysed using Xpert Highsore software and was indexed using Orifin 2025.XRD of the preheated sample is given below which shows presence of the compounds like K2NaAlF6, Na3AlF6, NaF.

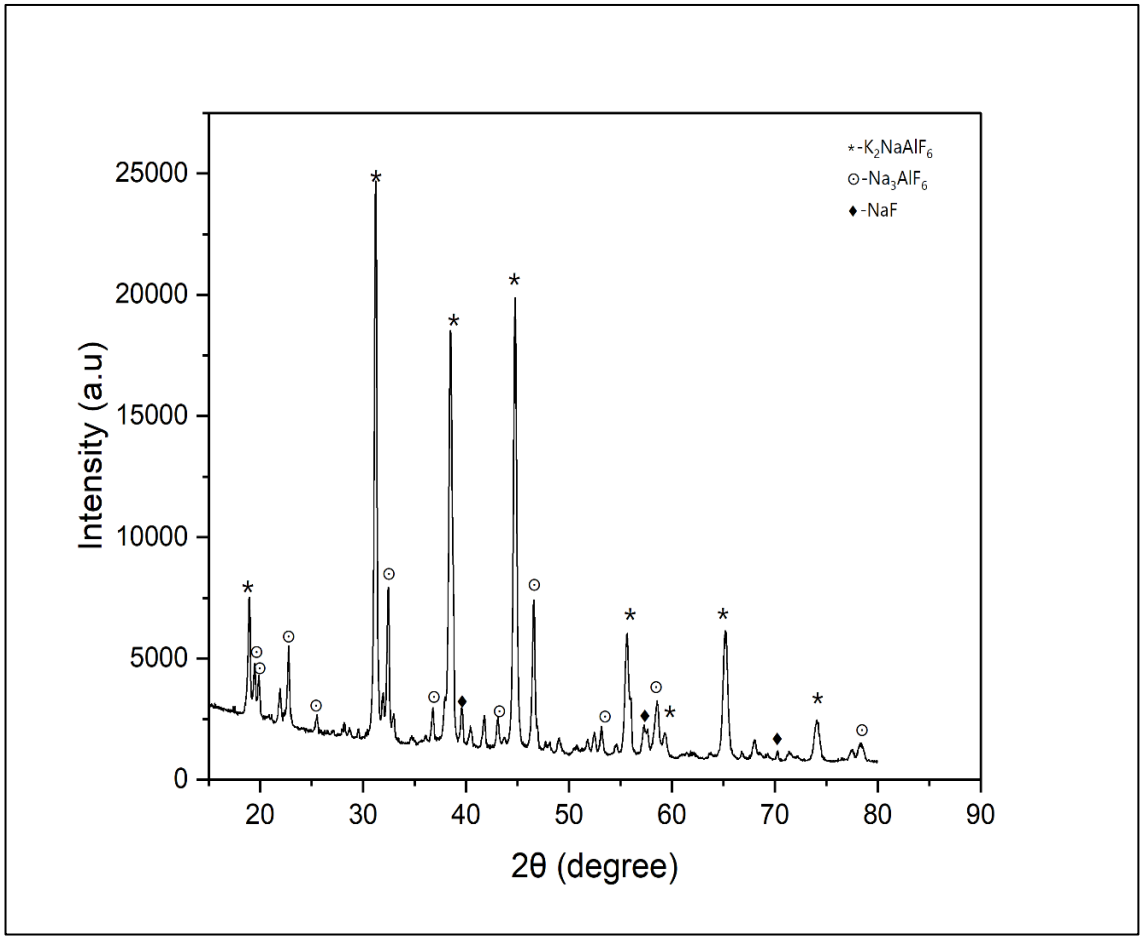

Figure 5.8 XRD Graph of the sample pre-heated to 1000 ºC

5.4 Bakelite-Sludge Composite study

A composite of Al-Bakelite is tried by mixing these two powders under temperature 160ºC but the results are not satisfactory as seen from fig 5.9. The cracks were observed in the Bakelite powder. Further, study in these regard is required. Further trials at higher temperature or higher pressure need to be explored.

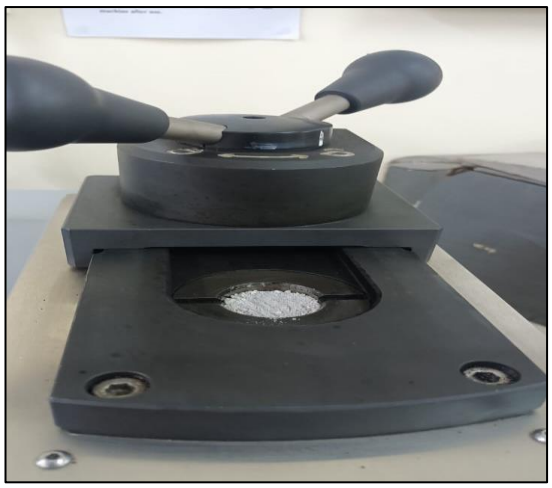

Figure 5.9.a Sludge before mounting in Bainmount Twin H auto Specimen mounting press

Figure 5.9.b Sludge after mounting in Bainmount Twin H auto Specimen mounting press

5.5 Study on Al -Sludge Composite

Microstructural study of Al- Sludge composite

5.5.1 Commercial Aluminium sample without the addition of sludge

The composite without the addition of sludge to commercial aluminium was studied. Its microstructure was revealed by Keller's Reagent. Under the microscope, the microstructure of the composite sample appeared as Figure 5.10.a before etching and after etching as Figure 5.10.b

Figure 5.10.a Optical image of sample with 0% sludge addition to Al before etching at 50x

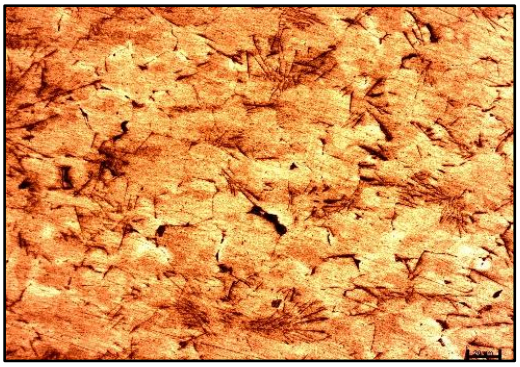

Figure 5.10 b a Optical image of sample with 0% sludge addition to Al after etching at 50x

.

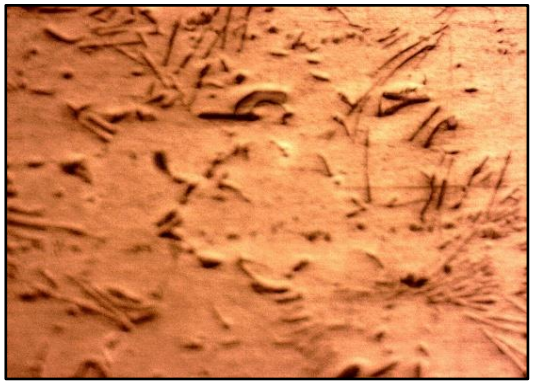

Figure 5.11.a Optical image of sample with 0% sludge addition to Al before etching at 100x

Figure 5.11.b optical image of sample with 0% sludge addition to Al after etching at 100x

Figure 5.12 SEM image of commercial Al sample

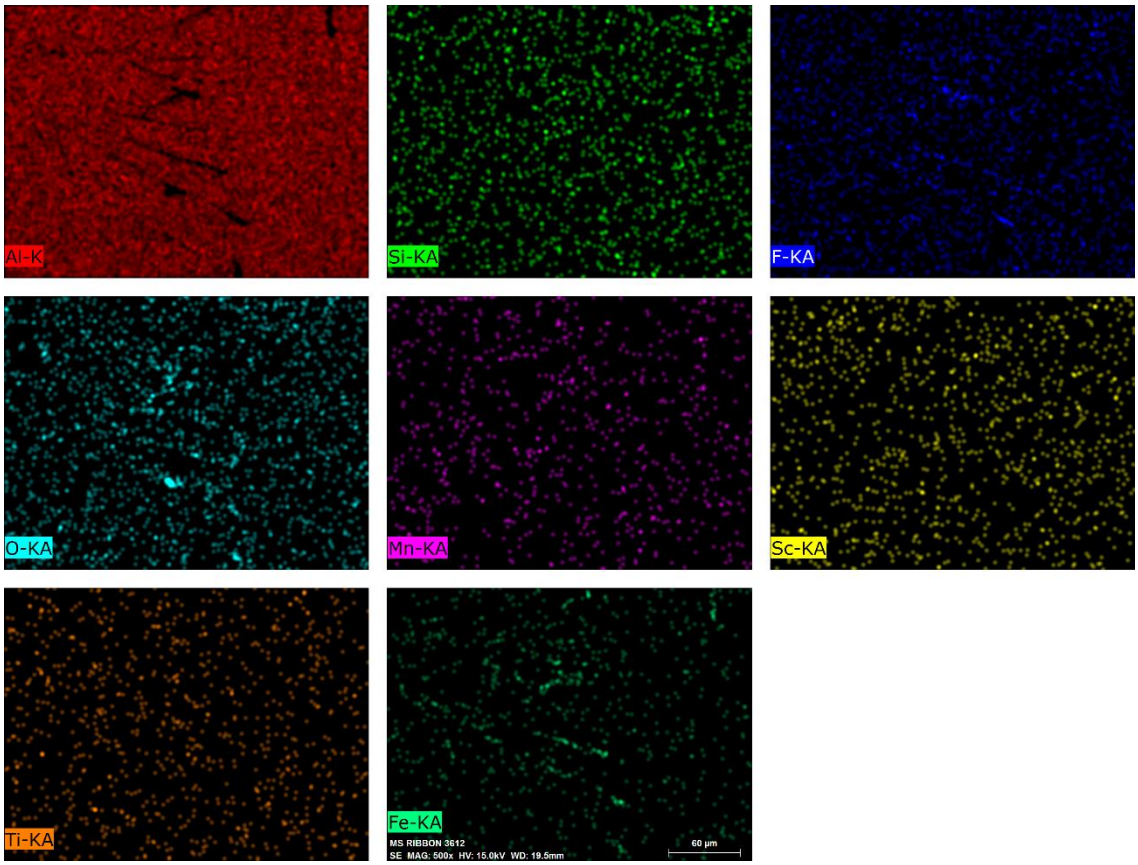

Figure 5.13 EDS images of the commercial aluminium sample.

The needle-like appearance in the microstructure was observed in SEM. Later, EDS was done to determine the elemental composition there. After EDS results analysis, it was found that the needles were enriched with Iron. The needle-like structure is called as "iron-needle." It negatively affects the Aluminium alloys' mechanical properties. In this case the $AlFe_3$ phase is observed at grain boundaries as found in commercial Aluminium alloys.

5.5.2 Commercial Aluminium sample with 10% addition of sludge

The composite with 10% addition of Sludge to commercial aluminium was studied. Its microstructure was revealed by Keller's Reagent. Under the microscope, the microstructure of the composite sample appeared as Figure 5.14.a before etching and after etching as Figure 5.14.b. .

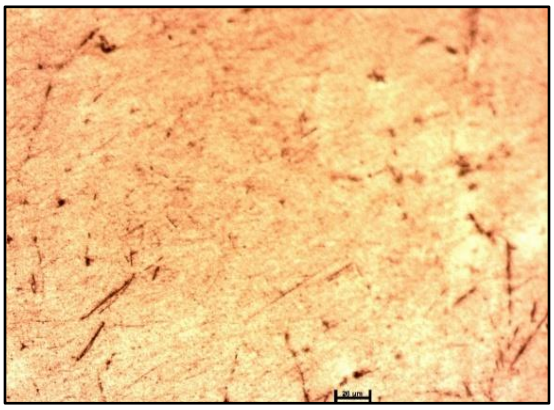

Figure 5.14.a Optical image of sample with 10% sludge addition in Al before etching at 50x

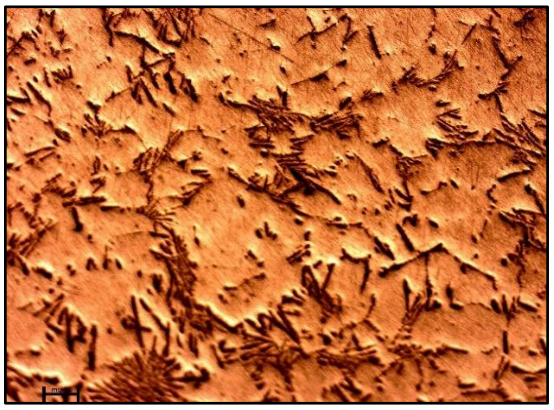

Figure 5.14.b optical image of sample with 10% sludge addition in al after etching at 50x

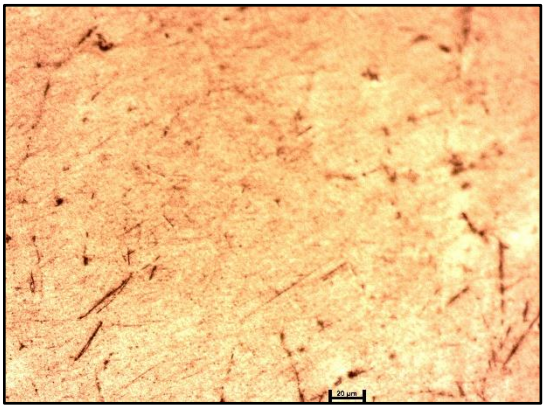

Figure 5.15.a Optical image of sample with 10% sludge addition in Al before etching at 100x

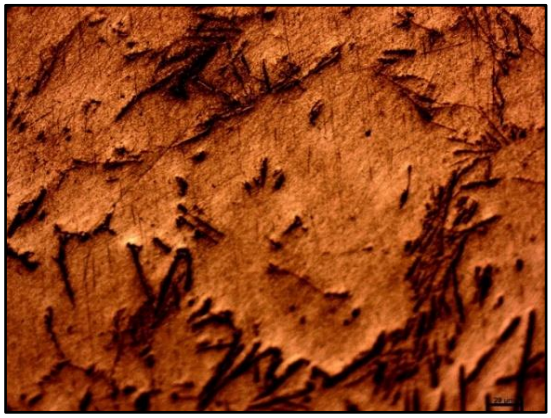

Figure 5.15.b Optical image of sample with 10% sludge addition in Al after etching at 100x

.

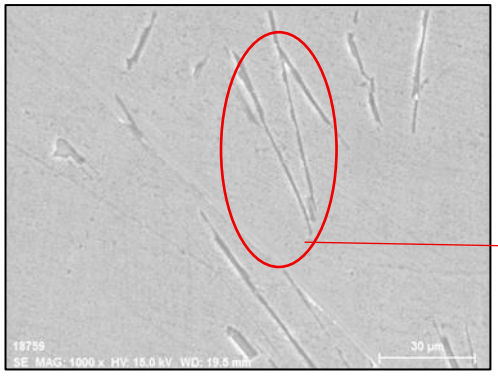

Figure 5.16 SEM image Commercial Aluminium sample with10% addition of sludge

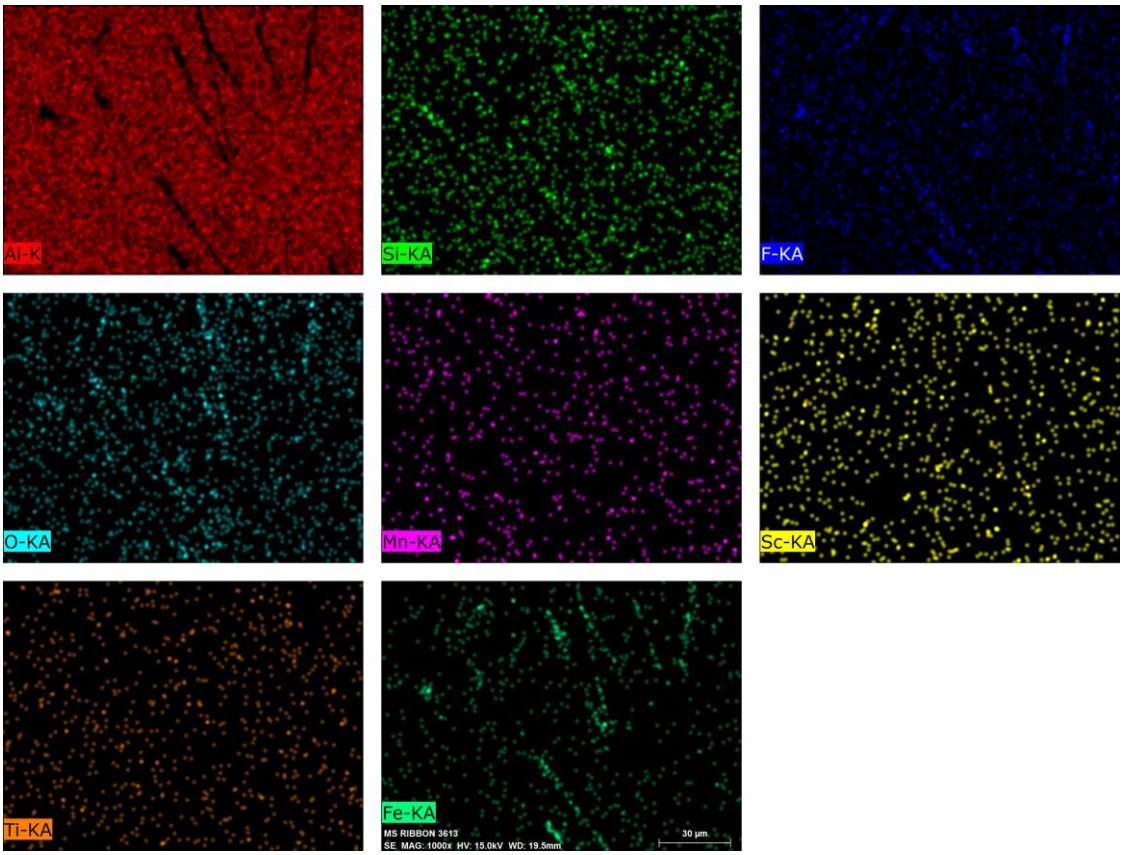

Figure 5.17 EDS images of Aluminium sample with 10% Sludge

The needle like appearance in the microstructure was observed in SEM also. Later EDS was done to know the elemental composition there. After EDS results analysis, it was found that the needles were enriched with the Iron and Silicon. Also some amount of Fluorine is found deposited in the needle like structure

5.5.3 Aluminium sample with 12.5 % addition of sludge

The aluminium composite with 25 gm addition of sludge was studied. Its microstructure were revealed by Kellers Reagent. Under microscope the microstructure of composite sample appeared as Figure 5.19.a before etching and after etching as Figure 5.19.b.

Figure 5.18.a Optical image of sample with 12.5% sludge addition to Al before etching at 50x

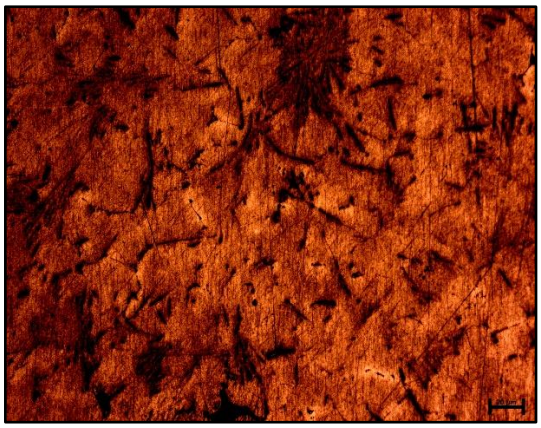

Figure 5.18. b optical image of sample with 12.5% sludge addition to Al after etching at 50x

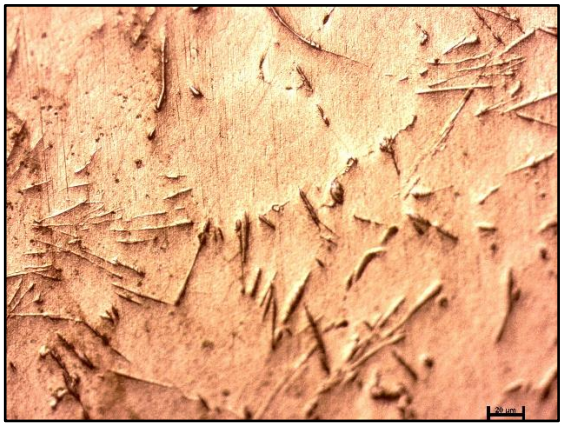

Figure 5.19.a Optical image of sample with 12.5% sludge addition to Al before etching at 100x

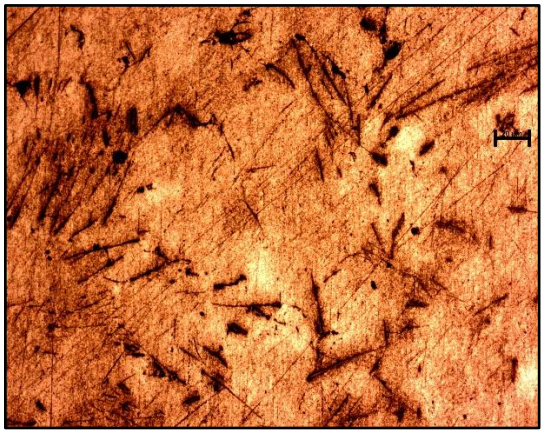

Figure 5.19.b Optical image of sample with 12.5% sludge addition to Al after etching at 100x

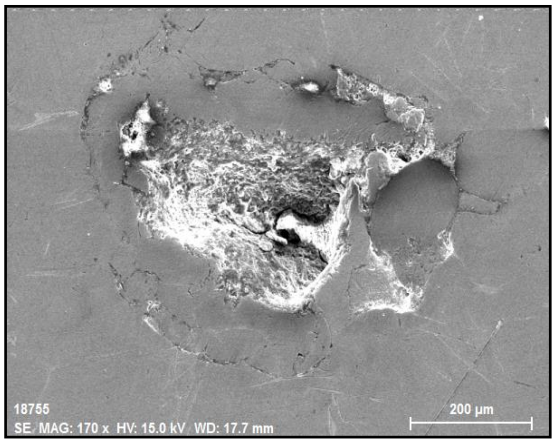

Figure 5.20.a SEM image of the segregate in sample with the 12.5% Sludge

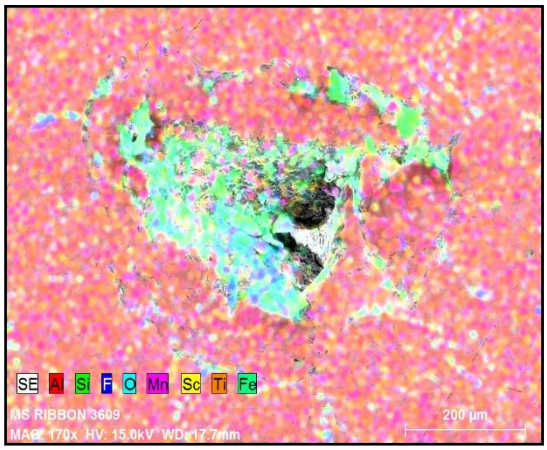

Figure 5.20. b EDS of the segregate in sample with the 12.5% Sludge

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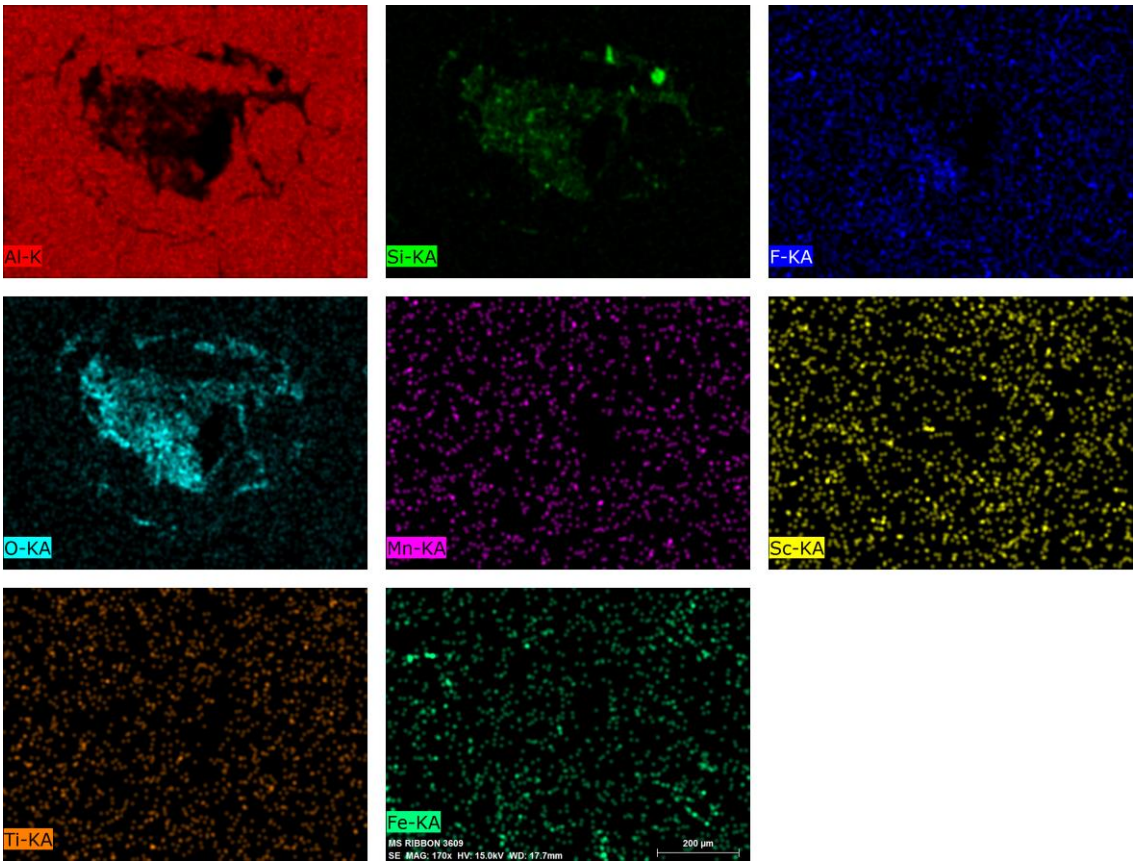

Figure 5.21 Elemental mapping of segregate in sample with 12.5% Sludge

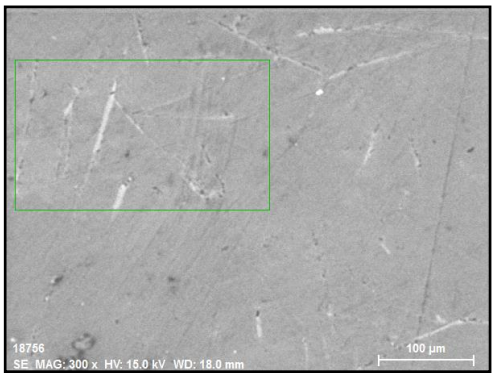

Figure 5.22.a SEM Image of Al-sludge composite with 12.5 % sludge addition

In the Figure 5.20.a we can observe a segregate whose EDS is shown in Figure 5.20. b. which shows the presence of the oxygen, Fluorine and Silicon.. These type of segregate are more common the sample with 12.5% sludge in Al.

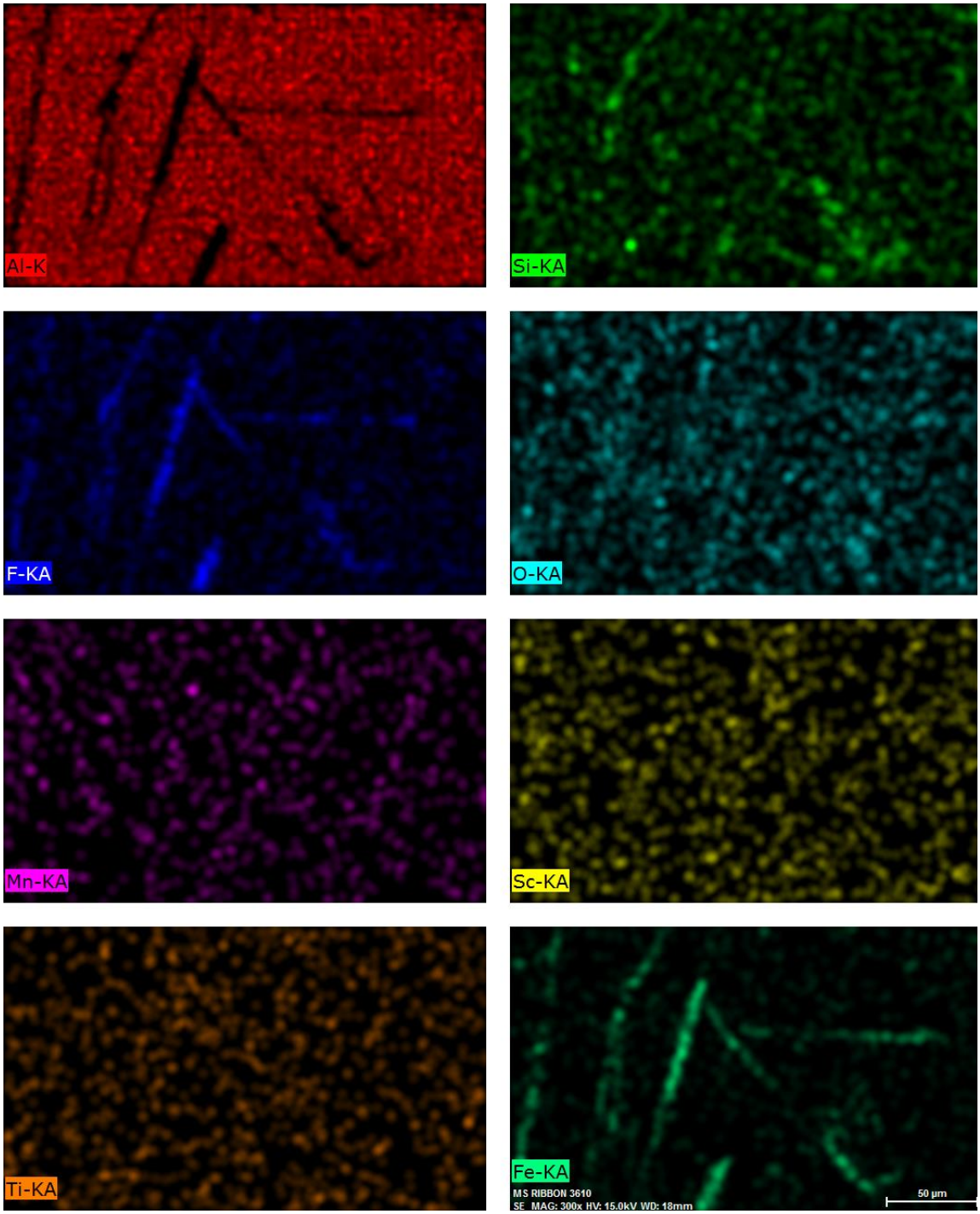

Figure 5.22.b Elemental mapping of the needle like structure on fig. 5.22

The needle-like appearance on the microstructure was observed in SEM. Later, EDS was done to know the composition. EDS results show the presence of Silicon, Oxygen and

Iron. There is an uneven distribution of the Fluoride from the sludge in the Al matrix. Also Fluorine was found deposited in needle like structure.

5.5.4 Effect of Sludge Addition in Al on Density

Table 5.5 Density Variation of Al- Sludge composite

SR.NO	SAMPLE	DENSITY(g/cc)
1	Commercial Al sample with 0% addition of Sludge	2.70723
2	Commercial Al sample with 7.93% addition of Sludge	2.6616
3	Commercial Al sample with 8.77% addition of Sludge	2.6344

A composite with low density is tried to prepare. It has inhomogeneous Fluorine distribution.

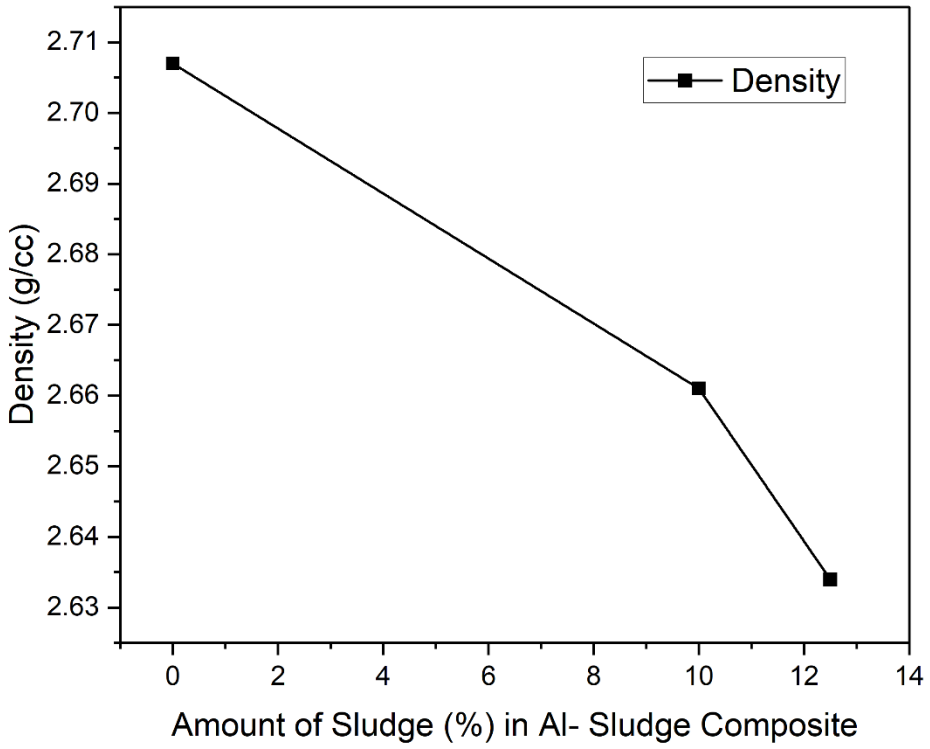

Figure 5.23: Effect on Density with the addition of Sludge in Al

Graphical representation of variation of density with the addition of sludge to aluminium is that with increasing addition of sludge density decreases. It may have two possible reason:

1) As low density sludge get mixed with the Aluminium, its density decreases
2)Due to the porosity created by sludge in Al matrix the density decreases of aluminium.

5.5.5 Study of Variation of Hardness with Addition of the Sludge to Aluminium

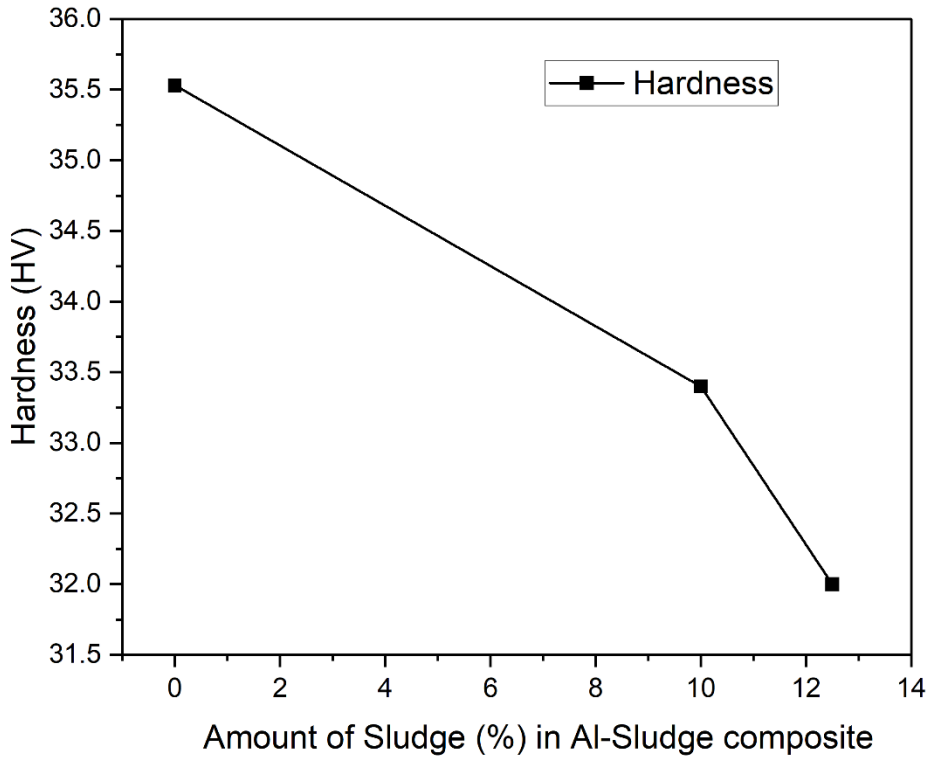

Figure 5.24 :Effect on the Hardness with the addition of Sludge in Al

From the graph shown in Figure 5.24 it is concluded that Hardness of the samples decreases as the sludge addition increases. This may have two possible reasons:
1)As most of the absorbed by metal is absorbed along the grain boundaries.
2)Hardness drop is observed due to the decrease in density.

SUMMARY AND CONCLUSION

The current work aimed to explore the useful potential of Fluoride rich Sludge so as to prevent fluoride containing Sludge from being dumped into the environment. Fluoride usually leach out into the ground through by mixing with water leading to various neurological and physiological disorders in human. Hence this study was carried out to find alternative ways to utilise this waste. The research also aimed at exploring the utility potential of the sludge in various fields. So, characterisation was done by various techniques such as XRF, XRD, SEM etc. Leaching Study was also carried out by dissolving sludge in different solvents. The study was also carried out by heating the sludge to 1000ºC to ascertain the thermal behaviour. Use of sludge for making composites by mixing with Al and bakellite powder were tried. Later the microstructure, hardness, density studies with the addition of sludge in the aluminium was done. Also the mass balance study is also done to track the efficiency of the process by considering certain assumptions. Certain conclusions are drawn from the above study and are listed below -

1)As the amount of Ti in TiBAl increases amount of K_2TiF_6 salt required also increases.
2)As the amount of Ti in TiBAl increases amount of KBF_4 salt required also increases.
3) Ratio of K_2TiF_6/KBF_4 increases, the amount of Ti in Master alloy.
4)The amount of Ti goes on increasing in master alloy the amount of TiB_2, Al3Ti goes on increasing.
5) PAF production increases as a result of increase in addition of halide salts K_2TIF_6 and KBF_4 which are added to increase the amount of Ti in the master alloy
3)The morphology of the sludge is mixture of cuboidal & cubical shape.
4)The compounds present in the sludge are K2NaAlF6, Na3AlF6, SiO2 and the material is highly crystalline.
5)From the table we can state order of solubility of the Sludge in solvents is as: HCl > H_2SO_4 > HNO_3 > H_2O > DMSO > THF.
6)The pH of the filtrate which we get after filtering the sludge solution is acidic and has pH value of about 4 and hence the potential use of Sludge to prepare the acid can be explored.

7) From XRD , colour and appearance of the sludge it is confirmed that Na_3AlF_6 dissociated into the NaF and AlF_3 on hesating the sludge to 1000°C.

8) Bakellite-sludge composite was not formed at 1 bar pressure and at temperature around 160ºC.

9) The density of Al-sludge composite is lesser than the Al sample

10). hardness is reduced due to addition of the sludge.

Future scope of study are listed below:

1)Searching for a solvent in the which sludge is soluble so as to separate the compounds present in sludge

2))Exploring ways to separate the compounds from the sludge by extractive metallurgy.

3) Exploring whether the application of sludge can be done as welding flux and fertilizer.

4)Interface study of Sludge and Aluminium in the Al-Sludge composite.

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